organic materials
and
soil productivity

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1. INTRODUCTION

Most of the industrialized countries are in the temperate zones of the world where a favourable balance exists between input and decomposition of organic materials in the soil. The conditions there cause a relatively high level of soil organic matter. This balance is influenced by climatic conditions and the inorganic constituents of the soil, in which the amount and type of clay minerals play an important role. The positive effect of mineral fertilizers depends upon well regulated humus husbandry. The plant growth caused by the use of mineral fertilizers increases not only the economically important parts of the plants, but also the growth of roots and crop residues which both remain on the fields and are ploughed into the soil. Furthermore, in many farms animal excreta is used to maintain the level of soil organic matter in arable land. There are some interactions between certain clay minerals and fractions of soil organic matter which act as favourable factors for soil productivity and therefore for plant production. This is not always the case in developing countries.

1.1 SOIL CONSTITUENTS AS FACTORS OF PLANT PRODUCTION

Plants are the basis of food for human beings and animals. If the energy from the sun, the content of carbon dioxide in the air, the amount and distribution of rainfall, the supply and the balance of inorganic nutrients are optimum, the growth of plants and therefore the yield of harvests depends upon the soil physical and mechanical properties as well as upon the chemical composition of the inorganic and organic soil constituents.

The properties of the inorganic part of soil are mainly influenced by the chemical composition of the parent material and weathering. The smaller particles, especially the colloid phase, determine the value of a soil for plant production more than the others. The mechanical properties of a soil, which influence gas exchange, water permeability, rooting of the plants, biochemical activity etc., are mainly caused by interactions between inorganic and organic soil constituents, mainly in the colloid phase.

In spite of the fact that the organic part of soil constituents is on average only from 0.1 to 5% of the dry matter of arable land, it influences the production capacity of soil to nearly the same degree as the inorganic. The organic part is formed mainly by biochemical transformations of residues of dead organisms living in and on the soil caused by microbial activity. The dynamics of these processes follow environmental conditions where climatic factors play the main role and it makes a difference if climatic conditions allow biochemical reactions to occur the whole year round or are stopped for a while in wintertime when temperatures are around $0^{\circ}C$ or below.

The main initial materials of soil organic matter are compounds of constituents of plants and micro-organisms or their metabolic products. Therefore, the more or less stable products of these processes, the humic substances, have in principle similar compositions. However, deviation in their composition occurs because of: different conditions during the humification of the organic materials, such as climate with its different temperatures or precipitation patterns; the actual composition of the inorganic soil components with its different amounts of nutrients and particle sizes; the degradability of organic material in the soil and the biological activity, which is determined by the first three factors mentioned. The characterization of the humic systems developed under the different environmental conditions by determination of physical and chemical data is therefore an important task for evaluation of the contribution of soil organic matter to the productivity potential of soils in different regions of the world.

1.2 DISTRIBUTION OF SOIL ZONES ON THE CONTINENTS

Two thirds of the earth are covered with water. The surface of the land zones consists of different soils, which have been formed by their environmental conditions.

Table 1   SOIL ZONES OF THE EARTH'S SURFACE

%

Arable lands

Temperate zones		Tropical and arid zones	
Soils of coniferous region	10%	Soils of humid tropical and subtropical region	19%
Soils of deciduous region	6%		
Steppe soils	12%	Soils of arid and semi-arid region	18%
Lowland soils	4%		
Total	32%	Total	37%

Zones without cultivated soils

Ice on the continents	11%
Tundra soils	4%
Mountain soils	16%

The nine different soil zones may be divided into three main groups:

30%	Land covered with ice, tundra soils, mountain soils	These zones are not suitable for agricultural food production.
32%	Soils of needle wood zone, the deciduous tree zone, the steppes and the lower land	These soil types occur mainly in the temperate zones. The arable land of these 4 soil zones is relatively rich in humus (average 3-5%). The climate is temperate and in wintertime no biochemical transformations occur.
		The most intensive agriculture is organized on these soils with the highest quantity of mineral fertilizers used and with an intensive humus husbandry.
37%	Soils of the arid regions and of the humid tropics and subtropics	In the arid zone natural vegetation is sometimes almost nil and in other parts very dense. Plants grow in subtropical and tropical regions all the year round. In some regions there is no rain or the distribution of rainfall is very unfavourable because it is heavy with short duration. The higher temperature enhances chemical and biochemical reactions in soil. Therefore, humus content is mostly relatively low (0.1-1.0%).

The two last mentioned soil zones with a total 37% are largely in the so-called "tropical belt" (30°N - 30°S latitude).

ICE CAP

ICE CAP

Arctic Circle

Tropic of Cancer

Equator

Tropic of Capricorn

Famine affected regions

Prairie Soils, Degraded Chernozem

Chernozems and Reddish Chestnut soils (with some inclusions of Dark Gray and Black soils of tropical savannas)

Dark Gray and Black soils of tropical savannas (with some inclusions of Chernozems and Reddish Chestnut soils)

Chestnut, Brown, and Reddish-Brown soils

Sierozems, Desert, and Red Desert soils (includes many areas of Lithosols, Regosols, and Saline soils)

Podzols and Weakly Podzolized soils

Gray-Brown Podzolic soils, Brown Forest soils, etc.

Latosols (Red Lateritic, Reddish-Brown Lateritic, etc.) and Red-Yellow Podzolic soils

Terra Rossa soils, mostly mountainous (includes many areas of Rendzina soils)

Soils of Mountains and Mountain Valleys (Complex)

Tundra

A   Alluvial soils (many small but important areas, not shown on map occur in all parts of the world)

No Symbol   Organic soils (Bog and Half-Bog) (many small areas, not shown on map, occur with Podzols, Weakly Podzolized, Gray Brown Podzolic, and Brown Forest soils)

By Charles E. Kellogg and Arnold C. Orvedal, adapted partly from Marbut, Glinka, and others, June 1956

AITOFFS EQUAL AREA PROJECTION
ADAPTED BY V. C. FINCH

Fig. 1   Distribution of soil zones on the continents and regions of insufficient food production (shaded)

Concerning their soil organic matter content only 6 main points are mentioned:

i. The higher temperature of the tropical belt in comparison to the temperate zones causes faster weathering of initial rock materials and their transformation products. Special soil types are formed: in the deserts only raw soils.

ii. In the arid region soils transport of salts and of sodium ions (chloride, hydrogen bicarbonate, etc.) occurs by capillary movement as a precursor of evapotranspiration. These processes retard plant growth and therefore humus dynamics.

iii. Most subtropical and tropical soils contain colloidal silicic acid hydroxylated iron and aluminium compounds. The heavy rainfall causes acute leaching of these and of soluble ions. If soils are not covered with plants transportation occurs of mainly colloidal material. Irrigation is practised in an attempt to compensate for the unfavourable distribution of rainfall for plant production.

iv. The naturally high level of plant production in the tropics is only possible because all organic dead plant material is recycled and transformed into humus. If this cycle is interrupted by cultivation and by moving nutritional plants from the fields, the balance between inorganic and organic soil constituents is disturbed. The interaction between these two is weakened, the texture decreases and erosion with its consequences occurs. Therefore, a humus husbandry must be practised.

v. The new high yielding varieties of cereals need greater fertilization with inorganic fertilizers and for the optimal economic yield. The higher dose of fertilizers not only increases the yield of grains, but also causes a higher activity of micro-organisms in the soil. However, many of these need carbon compounds as a source of energy, so the degradation of soil organic matter is accelerated and should be supplemented by organic materials. This supplementation may occur partly by higher production of plant roots or partly by addition of other organic materials such as crop residues, dung or prepared town waste products.

vi. The extent to which either mineral fertilizers and/or organic materials are used for plant production is a question of: a) economics, or b) special situation and availability.

These facts are the main reasons why humus husbandry as an important factor for plant production must be practised with adapted procedures. It seems that this is not always the case. It is not only the large increase in population in most countries of the tropical belt, but also the lack of utilization of all available production factors, e.g. humus husbandry, that causes insufficient food production in some regions (Fig. 1, shaded portions).

The effect of organic fertilizers was known in former times but due to the striking effect of mineral fertilizers the contribution of organic matter for plant production is at the moment less recognized and its proper use has been relatively neglected. Higher doses of nutrients are necessary to increase plant production per unit area. To obtain an increase in the efficiency of the added mineral fertilizers, an adequate supply of organic materials for corresponding humus dynamics is essential. Thereby physical, chemical and biological growth conditions and the stabilization of the yield potential of the soil are improved. The contribution of soil organic matter to environmental protection should not be forgotten either.

2. SOIL AS A SUBSTRATUM FOR PLANT PRODUCTION

The soil, which has been defined by Kubiena (1948, 1953) as "the transformation layer of the solid earth rind, inhabited by organisms, produced by the influence of life and the special environmental conditions of a biological habitat, subject to a particular annual change and a characteristic development," is today and will be in the future the most important substratum for plant production. It is formed by chemical, physical and biological weathering of the top layer of the parent material. The nature of soil formed depends on the following factors: parent material, climatic conditions, living materials on and in the soil (vegetation and soil organisms) topographical features, the time of formation and handling by man.

2.1 FACTORS AFFECTING SOIL FORMATION

The texture, hardness and composition of the parent material influence the texture, mineralogical composition and depth of the soil profile. Its mineral constituents act as a source of nutrients for living materials. The basic geological material is divided into igneous (solidified magma), sedimentary (deposited by water or wind) and metamorphic rocks (material from the first two types transformed by higher temperature and pressure). This basic material as well as that in all stages of disintegration is decomposed by different processes of weathering.

On climatic conditions depend the composition and intensity of life on and in the soil, which are major factors in the process of soil formation. Practically no soil formation takes place in cold regions where soil is frozen and there is little vegetation. With increasing mean temperature and higher vegetation, and also increasing soil micro-organism activity, soil formation and soil humus dynamics are enhanced. Lack of rainfall reduces soil formation, vegetation and the activity of organisms (e.g. in desert soils). With increasing rainfall, there is an increase in the rate of soil formation, but also there is leaching and erosion. In addition to the mean values of temperature and rainfall, their distribution during the year is also important.

Drainage (leaching) and erosion depend largely upon the topographical features of the soil surface. If the slope is steep, there is correspondingly greater erosion, consequently there are shallow profiles and younger soils on slopes, but the soils at the end of the slope are deeper and older.

Where there is no erosion by water and wind, the soil in time becomes deeper and more developed in the genetic sense.

The processes of chemical weathering of rocks and minerals are solubilization and hydrolysis. Water and oxygen, carbon dioxide and, to a greater or lesser extent, inorganic and organic acids solved in water are the agents. The products of solubilization and hydrolysis can be leached directly or after the formation of new, secondary products, which can be more or less soluble than the primary solubilized material, and are either lost by leaching or remain in the zone of weathering, e.g. clay minerals.

Physical weathering is the most important process in rock disintegration. Differences in daily or seasonal changes of temperature followed by expansion and contraction of the rock cause the initial cracking of the solid material. The velocity of disintegration depends on the degree of temperature variation and on the composition of the rock. Rocks with a coarse texture break more easily than finer textured ones and stratify more easily than homogeneous rocks. The effect of expansion and contraction is greater if the different kinds of minerals in a rock show bigger differences in reactability.

Freezing and thawing of water in the cracks of rocks breaks them up. The transport of rock material by ice (glacier) and water (river and surface water) reduces it to small pieces by milling during such transport and by abrasion with underlying material.

The best known process of biological weathering is the breaking of rocks through the expansion of roots entering cracks. The most important effect of biological life is the changing of the balance of solubility by uptake of ions and the secreation of more reactive compounds.

2.2 CHARACTERISTICS OF SOIL

The mineral composition of the parent material largely determines the content of minerals in the weathering product, soil. The chief minerals are quartz, feldspar and mica while accessory minerals are iron and aluminium oxides, carbonates and, in sedimentary rocks, clay minerals. But the more complete the process of soil formation and the stronger the weathering procedure, the greater is the shift to a relatively higher amount of less decomposable minerals and newly formed secondary minerals such as iron and aluminium oxides. Weathering removes the base elements of the parent material.

The texture of a soil is decided by the percentage of the particle size of the mineral part.
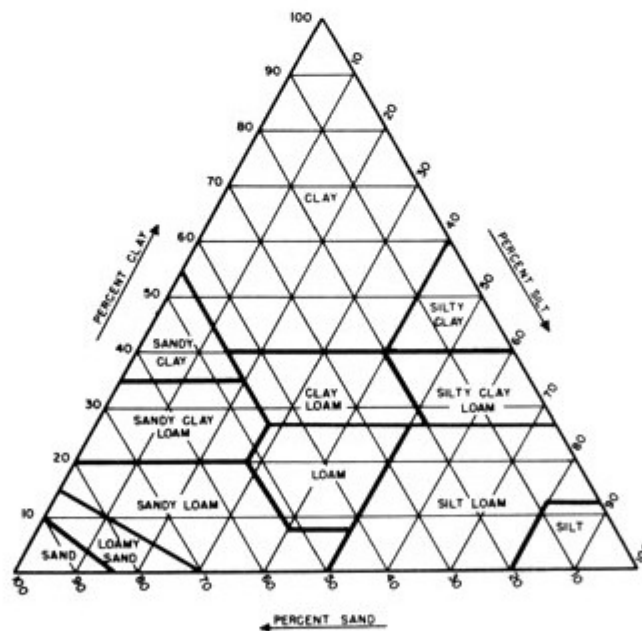
Fig. 2   Soil textural classes according to the percentage of clay (below 0.002 mm), silt (0.002-0.05 mm) and sand (0.05-2.0 mm). (USDA Handbook 18, Soil Survey Manual, 1951)

The diagram shows the importance of clay and silt in the classification of soil into textural classes. The productivity of soil increases with decreasing particle size, increasing surface area, water holding capacity and porosity until the soil becomes so fine that by poor aeration, unsatisfactory aggregation, slow water infiltration, poor drainage, diminution of root growth and reducing conditions, the productivity of the soil again becomes low.

The structure, i.e. the arrangement of the particles, of a soil depends on the size of its particles. Factors in the formation and destruction of structural units are the chemical and physical forces, e.g. wetting and drying, freezing and thawing, and handling by man. The organic matter in soil is a major factor in forming and stabilizing soil aggregates.

The porosity depends on the texture and on the structure of soil. A good soil structure determines the water and air regime and the development of roots in soil.

The surface area depends upon particle size, mineral species, exchangeable cations and the presence of organic matter, and the values given upon the method used for determination. The cation exchange capacity tends to vary directly with the surface area, but depends also upon the surface activity. Montmorillonite has the highest surface of the inorganic soil constituents with up to 800 m^2/g; kaolinite up to 30 m^2/g, the exchange capacity is about 130 resp. 8 meq/100 g, changing widely with particle size (Kelley and Jenny, 1936). The organic matter in the soil plays an important role in exchange capacity, depending on the quantity and quality of the organic matter. Some data are given in Table 2, according to Gorbunov (1948), on the portion of inorganic and organic soil components in the exchange capacity of different soil types (Flaig et al., 1963).

Table 2   EXCHANGE CAPACITY (e.c.) OF SOILS IN DEPENDENCY UPON THE PORTION OF INORGANIC AND ORGANIC SOIL COMPONENTS
(according to Gorbunov, 1948)

soil	horizon	% humus	e.c. total	% e.c. inorganic part	% e.c. organic part	rel. inorg. part	rel. org. part	e.c. in meq/100g mineral comps.	humus
strongly podzolic soil	Ap	2.82	10.08	7.22	2.86	71	29	7	101.5
	A2	0.66	6.16	5.24	0.92	90	10	5	140
mod. podzolic soil	Ap	3.24	12.56	7.07	5.49	56	44	7	170
	A1	2.74	12.02	6.74	6.28	56	44	7	230
slightly podzolic soil	Ap	5.29	26.54	14.65	11.89	55	45	15	225
	A1	5.34	23.09	15.07	8.02	65	35	16	150
slightly podzolic	Ap	6.13	35.29	13.69	21.60	39	61	15	350
dark grey soil	A3	4.97	34.09	15.46	18.63	45	55	16	375
leached chernozem	Ap	8.02	48.35	20.16	28.19	42	58	22	350
	A1	5.50	47.88	23.24	24.64	48	52	25	450
ordinary chernozem	Ap	7.90	56.86	25.68	31.18	45	55	28	395
	A1	5.96	52.91	25.00	27.91	47	53	27	470
southern chernozem	Ap	4.95	42.50	24.66	17.84	58	42	26	360
chestnut soil	A	2.07	16.68	8.60	8.08	65	35	9	390
grey soil	A	1.93	13.15	6.89	6.26	52	48	7	325

The most important chemical characteristics are: the soil's content of essential nutrients and their availability to plants, the exchange capacity, the buffering capacity, acidity or alkalinity, the content of inorganic and organic colloids, the quantity and quality of the organic matter, the oxidative or reductive conditions.

The amount and composition of organic matter in mineral soils is an extremely important factor influencing various chemical and biochemical processes going on in soil, its chemical, physical, physico-chemical and mechanical properties and its use in agriculture. The dynamics of the organic matter also have a significant effect on soil chemical, physical and biological processes.

The organic matter influences the soil fertility by participating in ion exchange reactions, by releasing nitrogen depending upon climatic conditions and micro-organism activity in the nitrogen cycle of soil processes, as a chelating reagent for the availability of metal cations to plants, by supplying biologically active substances and by stabilizing soil structure. The micro-organisms, which are of major importance in determining the dynamics of the organic matter, are dependent upon the amount and type of soil. The products of this biological activity include available nutrients and organic substances of different chemical composition and properties.

The favourable effect of the organic matter on soil structure enhances the rate of water infiltration, increases the water holding capacity and reduces run-off and erosion.

The complex system of the organic matter in soil can be divided, according to Kononova (1975), into diverse organic compounds, which are components of the soil organic matter.

Table 3   CLASSIFICATION OF ORGANIC SUBSTANCES IN SOIL

I. Fresh and incompletely decomposed plant and animal residues	II. Humus	
	(a) Strictly humus substances Groups: humic acids fulvic acids humins hymatomelanic acid	(b) Products of the advanced decomposition of organic residues and products of microbial resynthesis (substances of a protein nature, carbohydrates and their derivatives, waxes, fats, tanins, lignins, etc.)

Allison (1973, p. 34) estimates the amount of organic matter in living organisms. In micro-organisms it can be 0.1 to 2% of soil organic matter, which can be in all states of activity. It can be observed that in a very short time a resting state can change to an active state when humidity and temperature become better for the organisms. The animal population is likely to be greater in weight, but is less active than the microflora.

2.2.1 Soil Profile

The soil consists not only of the layer handled by man, for instance by ploughing. The growing roots, taking water and nutrients in deeper layers, the water movement and the transport of nutrients by water from the top to the bottom, or conversely, involve deeper layers of soil, which are often as important as the surface layer. This depth of soil is described as the soil profile. The terms A, B, C or D-horizon are commonly used to designate the significant different parts of a soil; the A-horizon contains mostly organic material formed in situ, the B-horizon weathered material usually without organic matter (with the exception of a horizon with enriched organic material transported from the top under the special conditions of podzolization), and the C or D-horizon the unweathered parent material.

2.2.2 Soil Types

Different soil types are formed depending upon the conditions for soil formation. The main zonal soil types are shown in Fig. 3.
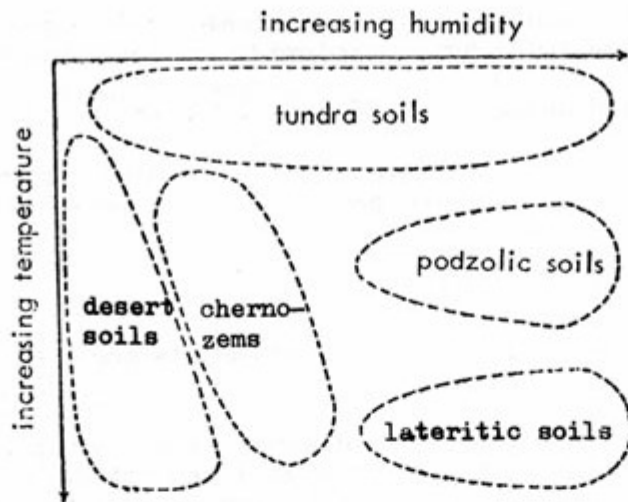
Fig. 3 Schematic diagram showing the broad geographic relationships
among the five major groups of zonal soils (according to Kellogg, 1953)

The influence of rainfall and mean temperature on the formation of soil
types and the amount of total carbon in Russian soils was shown by Tyurin (1937)
and the results of his research are given in Fig. 4.
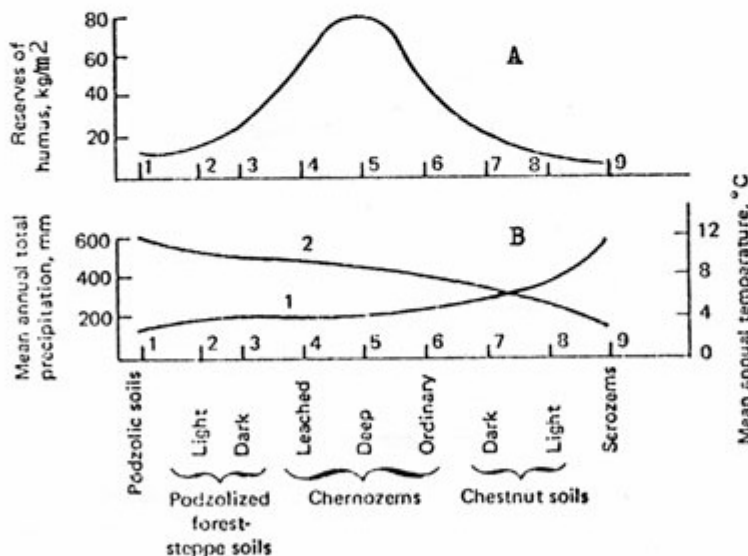
Fig. 4 Humus reserves and climatic conditions of the main soil types
and subtypes in the USSR (after Tyurin, 1937)

A   - humus reserves in soils to a depth of 100-120 cm in
       kg/m^2 of surface area;
B1 - mean annual temperature;
B2 - mean annual total precipitation

Jenny (1941) found a correlation between the climatic conditions and the
nitrogen content of natural soils, where the nitrogen content is a function of the

temperature during the year (T) and the quotient m calculated from rainfall in mm/ saturation deficit of the air in mm according to the following formula:

$$\% \text{ nitrogen in soil} = 0.55 \, e^{-0.08T} \, (1 - e^{-0.005 \, m})$$

Jagnow (1971) reported on a correlation between altitude, precipitation and cultivation, and the carbon and nitrogen content of East African soils.

2.3 MAN'S EXPLOITATION OF SOIL FERTILITY

Only a short review is given here as details are discussed later in specific chapters.

Under natural conditions an equilibrium is formed in the soil during the long period under prevalent climatic conditions and natural vegetation. The nutrient and humus levels remain almost the same, because exploitation and the loss of mature plant material are nearly nil. Conditions are changed drastically by man's use of the land. Decomposition of soil organic matter is enhanced by cultivation practices such as ploughing, mainly because of greater penetration by air. The return of organic matter to the soil is decreased by transporting the product from the field. The soil can also be damaged by erosion taking place from a bare soil surface during part of the year.
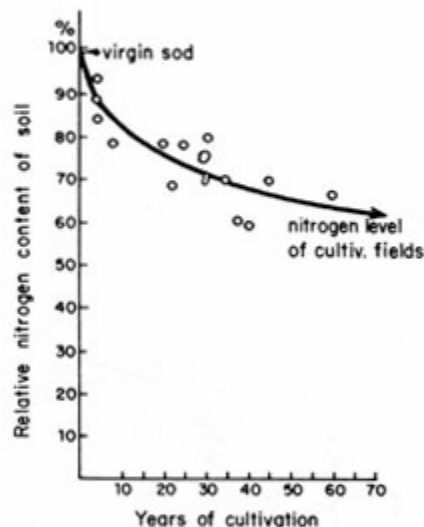
Fig. 5 Decline of soil nitrogen with length of cultivation periods under average farming practices in the Middle West (from Jenny, 1933)

Figure 5 shows the decrease of the nitrogen content in soil by farming practices in the Middle West of the USA. This means a loss of soil organic matter because about 97% of the nitrogen is bound in the soil organic matter in organic form. In Indian soils a greater decrease of soil organic matter was found - nearly 70%. This great loss was not only due to climatic conditions favourable to decomposition, but also to very small organic residues applied to the soil.

A new humus level is built up in the soil under cultivation, depending on the farmers' practices in addition to the natural factors mentioned earlier. Factors resulting from man's handling of the soil have various influences on the humus level in cultivated soils. The main effect, due to cultivation, is the higher input of air and the destruction of plant cover. According to Allison and Sterling (1949) losses of organic matter can be reduced by decreasing the number of cultivations and by

holding vegetational cover on the soil as long as possible, e.g. by replacing cultivated crops by sod crops. This procedure of fallow was used in agriculture in former times and nowadays there is wild rotation or minimum tillage of crops. In tropical conditions the regeneration of soil under uncultivated conditions and a vegetation cover is achieved by shifting cultivation.

The smaller the supply of organic material in the form of crop residues, due to a small yield or intensive removal of the grown yield, the greater is the decrease in soil organic matter. The decrease can be diminished by removing as little as possible and by increasing the yield, mainly of roots, by fertilization.

Compared with mineral fertilization alone, organic fertilizers maintain a higher humus level, but the effect of the organic fertilizer is dependent upon the decomposability of the added matter. Lignin-rich material is more slowly decomposed than lignin-poor material. The addition of readily available sources of organic matter to soil, such as green manure, in temperate climatic conditions, can result in a small increase of soil organic matter for a short time, but in warmer climates the decomposition is so rapid that the soil is not enriched (Anonymous, 1949). A negative effect from the addition of readily available organic material is observed if the decomposition of the native soil organic matter is accelerated (priming effect).

3. BIOCHEMISTRY OF SOIL ORGANIC MATTER IN RELATION TO SOIL PRODUCTIVITY

The biochemistry of soil organic matter concerns not only the formation and degradation of organic materials in soil but also direct and indirect effects on organisms living in and on the soil. The organic substances themselves and their interactions with the inorganic constituents of soil are important factors for the yield potential of soil.

In the last ten years the biochemistry of soil organic matter has made remarkable progress by combining improved techniques for physio-chemical measurements with the use of ^{14}C and ^{15}N and also ^{3}H (radioactive and stable isotopes).

The results of research work in the last two decades for elucidation of soil organic matter and its constituents in connection with their physical properties and their chemical composition, their phsyiological effects on plant growth as well as their importance for soil conditioning and therefore, finally, the influence of soil organic matter on plant production are described in various publications.[1]

Further information on this subject is available in abstracts from the congresses of the International Soil Science Society and the International Peat Society. Some data can be taken from publications by the International Biological Programme. There are also collections of literature for special problems in the annotated publications of "Soils and Fertilizers".

3.1 FORMATION OF SOIL ORGANIC MATTER

The content of soil organic matter in different soil types depends mainly on the climatic conditions, the plant cover and the properties of the inorganic part of the soil.

When one determines the content of humus dependent on decreasing average yearly rainfall and increasing temperature from the northern Tundra to the southern subtropics of the USSR, the percentage of humus increases at first and then decreases. From soil organic matter two main fractions can be separated by different extraction methods. The ratio of humic acids with high molecular weight substances to that of fulvic acids with mainly low molecular weight substances also increases at first and then decreases. The maximum effect in both cases is found in deep chernozem, which is a fertile soil. These results show that humification processes are influenced by different external conditions and that humus content differs widely between 0.5 and 10.0% per dry matter of soil. Recently Kononova (1975) published a review about humus content, its composition and the nitrogen reserves in different soil types.

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[1] Flaig, 1955, 1966; Scheffer and Ulrich, 1960; McLaren et al. (ed.), 1967; "Humus et Planta", 1961, 1963, 1965, 1967, 1971, 1975; IAEA/FAO (ed.), 1963, 1968; Kononova, 1966; Pontificiae Academiae Scientiarum Scripta Varia, (ed.), 1968; Sauerlandt and Tietjen, 1970; Schnitzer and Khan, 1972; Allison, 1973; Trojanowski, 1973; Orlov, 1974; FAO, 1975; Gieseking (ed.), 1975; Paul and McLaren (ed.), 1975 a, b; Povoledo and Golterman (ed.), 1975; Rabochev (ed.), 1975.
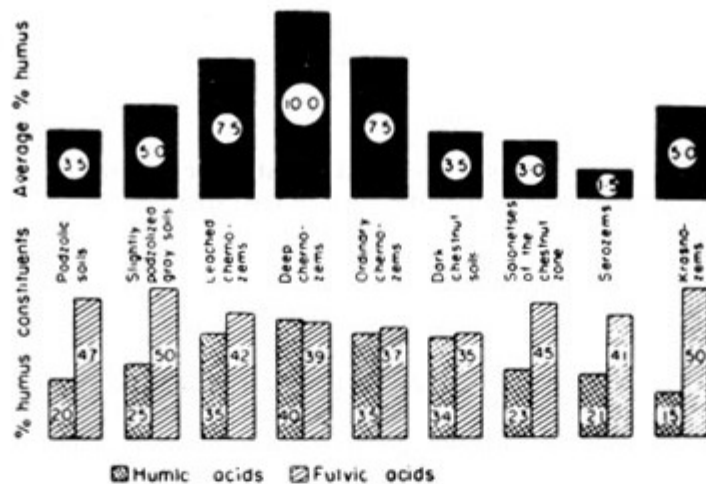
Fig. 6   Content and composition of humus in 0-20 cm layer of
                main USSR soil types (Kononova, 1966, cit. Tyurin)

          Experienced farmers are convinced that an equalized "humus husbandry"
(this means the addition of organic material to the soil and its transformation in
soils) plays an important role in soil productivity. Therefore they speak about
"humus effect". The causal connections for the success of such practices for
productivity or "faith of yield" of soils - as they say - are not yet completely
elucidated in this complex system, but it is important to find out the mode of action
for improving world food production.

          Most of the reactions for transformation of organic materials such as plant
residues after harvest, stable manure, excreta of animals and men, municipal
waste products, etc. are caused by microbial activity. In all cases the course of
the manifold reactions can be followed by labelling the initial material or inter-
mediate compounds with the isotopes carbon-14 and nitrogen-15.
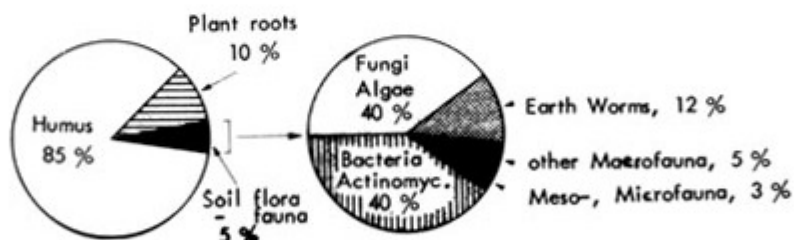
Fig. 7   Composition of organic substances in grassland soil
                (weight % of dry matter; according to Tischler, 1955)

          Some information about the composition of organic substances in a grass-
land soil is given in Fig. 7. The dead material, the humus, is 85%, the living
constituents are plant roots 10% and soil flora and fauna about 5%. Most trans-
formations of dead materials occur through the activities of soil organisms. The
soil flora and fauna consist of 12% earth worms, 5% other macro-fauna and 3%
meso and micro-fauna. These groups of living organisms participate more in
mechanical processes to reduce dead materials to small pieces than in chemical
ones. Most biochemical reactions are initiated by the 40% of fungi and algae on

the one side and by the 40% of bacteria and actinomycetes on the other. The metabolic activity of fungi is greater than that of bacteria in the transformation of organic materials of dead organisms (Anderson and Domsch, 1975). New compounds are also formed by the metabolism of micro-organisms, which play an important role during humification and in the soil fabric.

One of the most important sources of nitrogen in nature is the humic system; other elements necessary for plant nutrition are formed by the weathering of minerals.

Present knowledge of the synthesis of humic substances can be summarized in a scheme (see Flaig et al., 1975; Martin and Haider, 1971 and others).
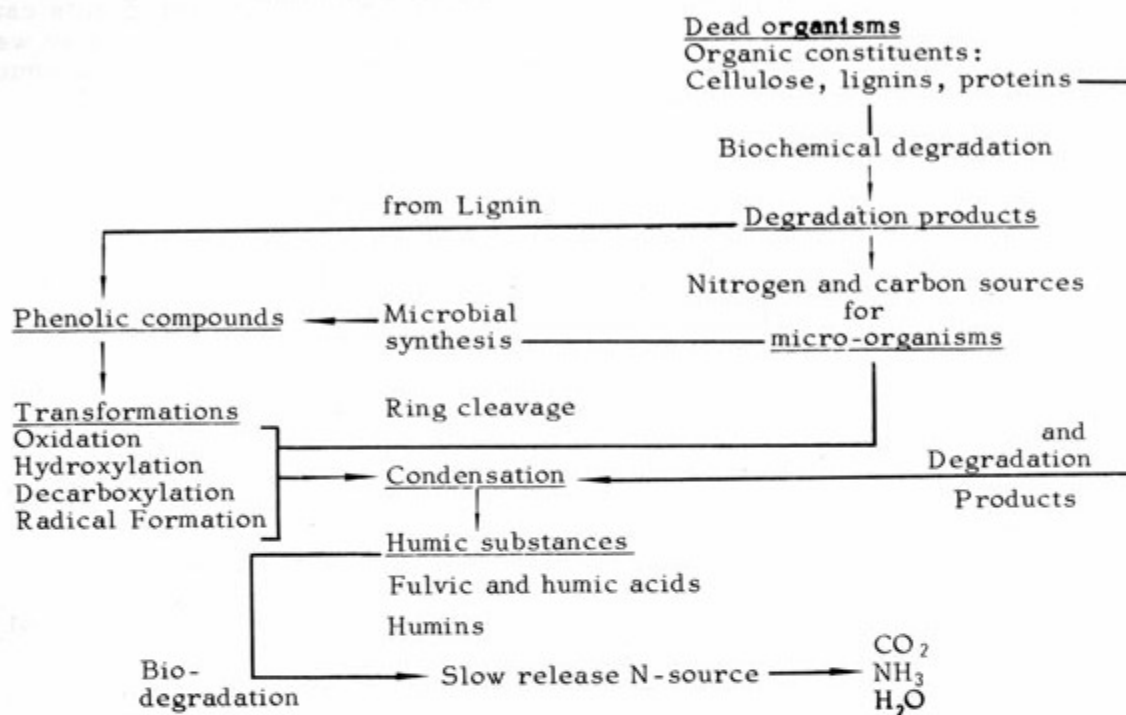
Fig. 8   Scheme of synthesis of humic substances from transformed organic constituents of organisms

The main organic constituents of the dead organisms in soil are cellulose, lignins and proteins. By biochemical degradation different products are formed which serve the micro-organisms as carbon and nitrogen sources, mainly cellulose and proteins. Different phenolic compounds are formed from lignin. Microbial synthesis is another way of forming phenolic compounds. These types of phenolic substances are mainly transformed by oxidation, hydroxylation and decarboxylation. During these transformations ring cleavage also occurs and aliphatic compounds are formed, which are used by the micro-organisms as carbon sources.

During the transformations of the phenolic substances free radical formation also occurs. These radicals condense with degradation products of proteins to humic substances. The humic substances are separated by conventional methods into fulvic and humic acids and into humins. The humic substances have influences, together with humified plant materials and other newly formed compounds, on the physical properties of soil and on the pathways of plant metabolism by their physiological activity after uptake by the roots. The biodegradation of humic substances in soils is slower than that of the initial materials, from which they are formed (Sauerbeck, 1968 a, b, a; Sauerbeck and Führ, 1970). During these processes soil organic matter acts as a slow release nitrogen source for plant nutrition during growth.

Finally the humic substances are degraded to carbon dioxide, ammonia and water. The formation and degradation follow a dynamic course, which is influenced by climatic factors, vegetation and composition of the mineral part of soil.

3.2   INFLUENCE OF SOIL ORGANIC MATTER ON PLANT GROWTH

There is a differentiation between indirect and direct effects of humic substances on growth and yield of plants (summary in Flaig, 1968). Humic substances, mainly the high molecular weight part, can effect changes in the environment of the roots by changing physical and chemical properties such as water holding capacity, gas exchange and others, which lead to better growth of plants. In the final stage there is an increase in yield of crop plants caused by these indirect effects. The indirect effects caused by high molecular weight substances will be discussed in Chapter 4 in connection with the influence of naturally occurring polymers in the soil fabric.

indirect
effects

direct
effects

humic substances   humic substances

Influence on chemical
and physical properties
of the soil

Influence on metabolism
after uptake by the plant
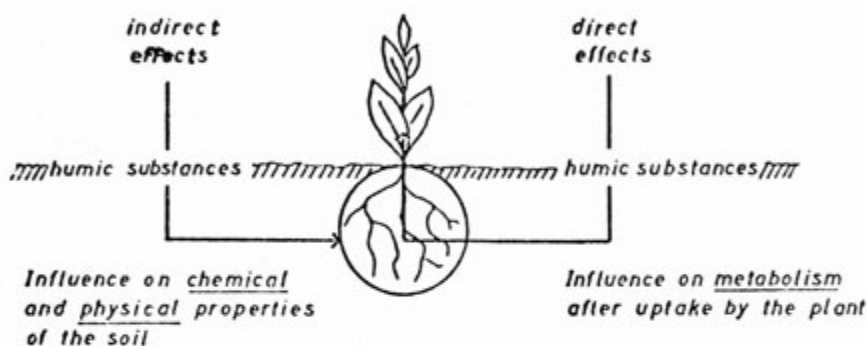
Fig. 9   Scheme of the possible effects of humic
                     substances on growth and yield of plants

Direct effects are those caused by the uptake of low molecular weight organic compounds from soil organic matter. They bring about alterations in plant metabolism.

At present, phenolic compounds are known mainly as substances which are efficient yield increasers; they are compounds formed by lignin degradation or microbial synthesis. In the presence of phenolic compounds instances of increased resistance by plants to frost or drought and other effects have been observed. By experiments it was demonstrated that favourable effects occur mainly when growth factors such as temperature, humidity, oxygen tension in the soil air, etc., are under optimum or the ratios of nutrients are unbalanced.

Indirect and direct effects have a special influence on the yield potential of different soils which cannot be explained by the availability of plant nutrients. Similar observations are made by farmers when the content of soil organic matter reaches a certain level and the transformations follow corresponding dynamics. In both cases the activities of man can interact.

3.3   DEGRADATION OF PLANT CONSTITUENTS (STRAW) DURING ROTTING

Straw is one of the most important rural wastes. The transformation of its constituents has been studied under different conditions. Straw is relatively rich in cellulose and lignin but poor in protein; summarily, one can say that the rate of decomposition depends on the possibility of growth conditions for the micro-organisms which participate in transformation of cellulose and lignin.

Normally if nitrogen is low, the decomposition rate is slow; in some cases also if the soil moisture is low the decomposition is again slow. This is a major problem and it is difficult to accelerate decomposition in arable land during crop rotation. Further research in this field is necessary, especially in connection with the soil's nitrogen cycle. Some fundamental publications are given in the footnote.[1]

During rotting of straw the cellulose is degraded much faster than lignin. The available nitrogen is a limiting factor for micro-organism activity. The rate of cellulose degradation is more enhanced that that of lignin if nitrogenous compounds, such as ammonium nitrate, are added. This means that lignin participates more in humus dynamics than cellulose.
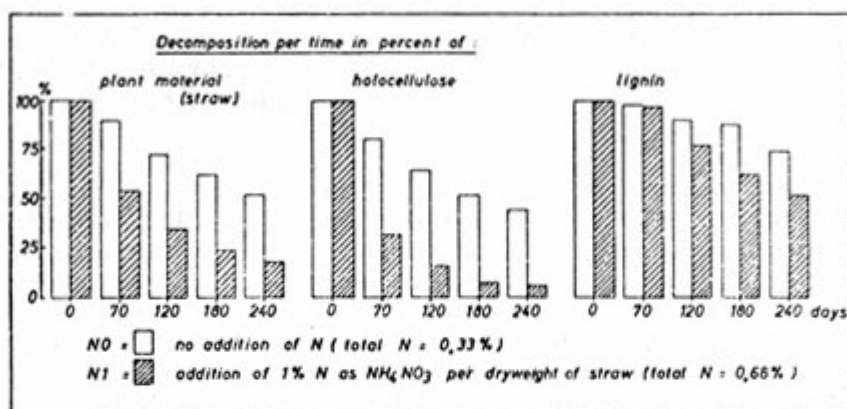
Fig. 10   Decomposition of plant material (straw), holocellulose and lignin in percent during rotting time (Maeder, 1960)

Table 4   CHANGES IN THE NITROGEN AND METHOXYL CONTENT OF LIGNIN IN RYE STRAW DURING ROTTING TIME (addition of 1% N as NH_4NO_3 per dry weight of straw) (Maeder, 1960)

Days	N %	OCH$_3$ %
0	0.53*	17.08
70	1.44	12.76
120	1.68	11.33
180	1.74	10.95
240	1.88	10.46

*   initial value

---

[1]   Bartlett and Norman, 1938; Bartlett, Smith, Brown, 1937; Broadbent, 1954; Flaig, Schobinger and Deuel, 1959; Kaila, 1952; Kononova, 1966, et al. 1973; Maeder, 1960; Mohtadi, 1962; Phillips, 1934; Reinhardt, 1961; Schobinger, 1958; Smith, Stevenson and Brown, 1930; Springer and Lehner, 1952 a, b; Waksman, Tenny and Diehm, 1929; with labelled material e.g.: Führ et al., 1964; 1965, 1966, 1968; Guckert et al., 1971; Jansson, 1968; Jenkinson, 1965, 1966 a-d, 1968, 1971; Martin et al., 1974; Mayaudon et al., 1958, 1959 a, b, 1960, 1961, 1963; Oberländer, 1968; Sauerbeck, 1968 a-c, et al., 1968, 1970; Scharpenseel, 1960 a, b, 1966, 1970, et al., 1962, 1964; Simonart et al., 1958 a, b, 1959 a, b, 1966, 1968; Sörensen, 1963, 1966.

In the lignin fractions isolated with sulphuric acid the content of nitrogen increases concurrently with the time of rotting, whilst the methoxyl content decreases.[1] This suggests that the cleavage of the methoxyl group preceeds the introduction of nitrogenous groups in the lignin degradation products (Flaig, 1960 b). Part of the fixed nitrogen becomes less available for micro-organisms by these procedures. This part of organic bound nitrogen plays an important role in the nitrogen economy of the soil-plant system and belongs to the reservoir of slow release nitrogen in the soil. The demethylation of lignin is enhanced by the addition of nitrogenous salts because of higher microbial activity. The degradation of synthetic lignins by different micro-organisms was intensively investigated with labelled products (Haider and Martin, 1967, 1968).

Different lignin types have been synthesized with monomers labelled with different carbon atoms by Freudenberg's mushroom phenol oxidase method (1962, 1964 a, b). By measuring released active carbon dioxide it was possible to identify single steps of lignin degradation during humification (summarized in Martin and Haider, 1971).

According to present knowledge, the biochemical degradation of lignin occurs by the splitting of ether linkages in the high molecular weight molecule. Lower molecular weight particles are formed. During these oxidative processes cleavages of the aromatic rings of the monomers occur. Aliphatic compounds are formed which serve as the carbon source for the micro-organisms. Phenolic compounds can also be isolated as degradation products from humified plant material (Maeder, 1960; Flaig, 1962), from peat (Belav, 1967; Söchtig and Maciak, 1971) or from soils (Bruckert, Jacquin and Metche, 1967; Schnitzer, 1972 and others). These compounds are of interest from different points of view in the biochemistry of humic substances. It is known through laboratory experiments that they react under oxidative conditions with nitrogenous compounds such as amino acids, ammonia and others by forming substances which are very similar to humic acids isolated from soils (summarized in Flaig, 1975). Furthermore, it was demonstrated that some of these compounds can be taken up by plants through the roots. The compounds and their oxidation products (quinones) influence the metabolism of plants (summarized in Flaig, 1968).

In this field further research should be done because not all causal connections about the influence of phenolic or quinonoid compounds on metabolism and the yield of plants are known yet, but some will be mentioned in a later paragraph.

3.3.1   Lignin Degradation

The biochemical transformation of the phenolic lignin degradation products was investigated with differently labelled compounds (Haider, Lim and Flaig, 1962, 1964; Haider, 1965). The main reactions are summarized in Fig. 11.

The most essential transformations of lignin degradation products are:

i.   the shortening of the side chain of phenol acrylic acids and formation of phenol carboxylic acids;

ii.   demethylation of phenol ether to phenol carboxylic acids with hydroxyl groups in ortho-position (i.e. transformation of vanillic acid to protocatechuic acid);

---

[1] Bartlett, 1939; Bartlett and Norman, 1938; Broadbent, 1954; Flaig, 1960 a; Flaig, Schobinger and Deuel, 1959; Nehring and Schiemann, 1952; Ritter, Seborg and Mitchell, 1932; Stöckli, 1952; Waksman and Smith, 1934.

Lignins

OH OCH₃ H₃CO OCH₃ OH
ferulic -   sinapic -   p-coumaric acid
CH   CH   CH
‖   ‖   ‖
CH   CH   CH
COOH   COOH   COOH

Shortening of the Side Chain and Oxydation

OH OCH₃ H₃CO OCH₃ OH
vanillic -   syringic -   p-hydroxy—benzoic acid
COOH   COOH   COOH

Demethy-
lation   Hydroxylation

keto   Ring
acids   cleavage
OH OH   HO OH OH
COOH   COOH
protocatechuic-   gallic acid
Oxydative Decarboxylation

OH OCH₃   H₃CO OCH₃   Dimerisation
                             Polymerisation
OH   OH
methoxy-   2,6 - dimethoxy-
               hydroquinone

Fig. 11   Transformation of lignin degradation products

iii.   hydroxylation of phenol carboxylic acids to such acids with hydroxyl
        groups in ortho-positions (i.e. p-hydroxy benzoic acid in protocatechuic
        and gallic acid);

iv.   the oxidative decarboxylation to hydroquinone derivatives (i.e. the
        transformation of vanillic acid into methoxy-hydroquinone);

v.   the cleavage of the ring in the case of phenol carboxylic acids with
        hydroxyl groups in ortho-position to aliphatic keto-acids;

vi.   dimerization and polymerization reactions under oxidative conditions by
        formation of intermediate quinonoid products.

3.4 MICROBIAL SYNTHESIS OF PHENOLS AND THEIR PARTICIPATION IN THE FORMATION OF HUMIC SUBSTANCES

Several soil micro-organisms synthesize phenols in their metabolism which
participate in the formation of humic substances (summarized in Martin and Haider,
1971; Haider et al., 1975).

After the addition of ^{14}C-labelled glucose or cellulose to a soil, several
phenols could be isolated from the extracted humic acids by reductive cleavage with
sodium amalgam (Martin et al., 1974) after 2 or 3 weeks. The phenols contained
the major portion of activity. So it was proved that the phenols were synthesized
by micro-organisms from aliphatic precursors (Fustec-Mathon et al., 1973). The
properties of the microbially synthesized, humic acid-like substances are com-
parable to those isolated from soil as was demonstrated, for instance, by infrared
spectra (Filip et al., 1974).

The formation and transformation of the microbially synthesized phenols were followed by different procedures. Most phenols formed in this way belong to 1.3-di- or 1.3.5-triphenols, but by degradation of lignin phenols have been formed with hydroxyl groups in the 1.2 or 1.2.3-position, which have been partly methylated.

For instance in the case of Epicoccum nigrum orsellinic and cresorsellinic acid is formed (Haider and Martin, 1967). The following scheme demonstrates the main reactions, occurring in culture solution, from which the corresponding compounds were isolated. Most of them were also identified in the formed humic acid-like substances after reductive cleavage with sodium amalgam.
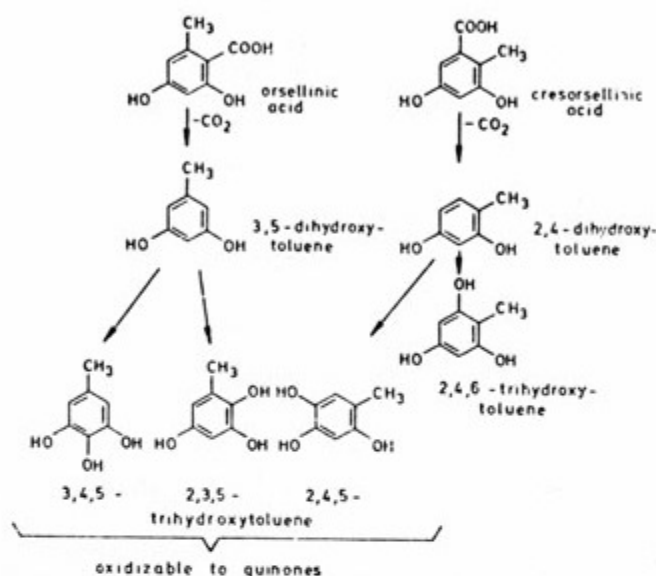
Fig. 12 Synthesis of phenols by micro-organisms and their transformations
(Epicoccum nigrum)

The transformation of the metabolically synthesized orsellinic and cresorsellinic acid occurs by:

i.   decarboxylation

ii.   hydroxylation

iii. oxydation of methyl group to carboxyl group and again decarboxylation.

The third reaction is not especially mentioned in the scheme, although polyphenols, such as resorcinol and others, could be identified.

Most of the microbially synthesized phenols have two or three hydroxyl groups in m-position. Therefore, nucleophilic addition of compounds cannot occur before reactive phenols are formed by hydroxylation into compounds with hydroxyl groups in o-position. The compounds with hydroxyl groups in o- or m-positions differ widely in their reactivity. Catechol, pyrogallol and hydroxyhydroquinone derivatives add nucleophilic derivatives of resorcinol and phloroglucinol (Musso et al., 1965), or proteins or their products of hydrolysis during oxidation, to quinonoid intermediates. The oxidative coupling between the phenols leads to ramification and increases aromaticity. The differences in reactivity of the two phenol types are important with respect to the function of nitrogen in the molecule of humic substances. This means that, in general, compounds which are able to form quinones are important for the formation of nitrogenous humic substances.

Phenolic compounds formed by degradation of lignins or synthesized by micro-organisms were identified after oxidative or reductive cleavage of humic acids isolated from soils (Burges, Hurst and Walkden, 1963, 1964; Morrison, 1963; Farmer and Morrison, 1964; Martin et al., 1974 and others). These results are of interest in studies about the structure and also the chemical and physical properties of humic acids (see scheme of formation of humic substances, Fig. 14).

3.5 MODEL EXPERIMENTS ON STRAW DECOMPOSITION FOR PROCESSES OCCURRING IN NATURAL CONDITIONS

Further experiments have been made on the decomposition of lignin-containing material, such as wheat straw, to explain processes which may occur in nature. For instance, sterilized straw was incubated: i) by pure cultures of soil fungi of different systematic groups, which synthesize phenols in their metabolism, and ii) by pure cultures of basidiomycetes, which do not synthesize phenols. Both types of strains degrade lignin. In total 19 strains were investigated (Grabbe and Haider, 1971).

The following observations were made:

i. Results which are the same in both cases

    a. after 4 months 25 - 45% of the lignin was degraded in both cases;

    b. after the same incubation time a decrease in the methoxyl content of the isolated lignin fractions by 50 - 60% occurred;

    c. nitrogen was fixed to a larger amount in the high molecular weight fractions of lignin and humic acids; 30 - 40% of this nitrogen can be hydrolized by 6 M HCl (nitrogen was added as asparagine to the culture media).

ii. Different results in both experiments

    a. the production of humic substances was lower in the case of the incubation with non phenol synthesizing strains;

    b. the chemical structure of phenols in the fraction of humic acids was different in both cases. The phenols were determined by reductive cleavage with sodium amalgam according to Burges et al. (1963, 1964; compare: Piper and Posner, 1972 a, b; Martin et al., 1974).

       - in the case of fungi, which synthesize phenols, lignin-derived as well as microbially synthesized phenols are found after reductive cleavage with sodium amalgam in the humic fractions and fractions of rotted lignin. This means that humic acids are formed by condensation of phenols derived from lignin and microbially synthesized phenols. It seems, furthermore, that also degraded lignin reacts with microbially synthesized phenols.

       - phenols derived mainly from lignin were identified by inoculation with basidiomycetes - non phenol synthesizing organisms.

In further laboratory experiments the formation of humic acids was studied with labelled materials in 3 different ways (Martin et al., 1974):

1) ^{14}C glucose was added to a fertile garden soil and incubated 6 weeks. Afterwards the humic acid fraction was isolated, treated with sodium amalgam, the phenols separated by two dimensional thin layer chromatography and the ^{14}C activity was determined for each spot in the chromatogramme. About 16 phenolic compounds were identified;

2)   uniformly ^{14}C labelled straw was added to the same soil and incubated 6 weeks. After the same procedures the ^{14}C activities of the separated phenols were determined;

3)   in the last experiments the soil was sterilized with ethylene oxide, inoculated with <u>Stachybotrys chartarum</u> (a fungus which synthesizes humic acid-like substances in culture media) and amended with ^{14}C glucose.

      The data of the experiments are summarized in Table 5. By adding ^{14}C glucose the radioactive phenols could be synthesized only by micro-organisms. Smaller amounts of lignin derived phenols with methoxyl groups are synthesized mainly after the addition of uniformly labelled straw. The amount is small because, as mentioned before, demethylation occurs during lignin degradation.

Table 5   DISTRIBUTION OF ACTIVITY IN PHENOLIC COMPOUNDS FROM HUMIC ACIDS AFTER ADDITION OF LABELLED MATERIALS TO A SOIL UNDER DIFFERENT CONDITIONS
(according to Martin <u>et al.</u>, 1974)

Added Materials	Unsterilized soil		Sterilized soil
	UL[14]C glucose	UL[14]C straw [" cellulose " lignin]	UL[14]C glucose
	Usual microbial population		Stachybotrys chartarum (inoculated)
Activity in humic acids in percent of that applied (Activities in phenols were 7-10% of activity in humic acids)	14% [1]	13%	15%
Microbially synthesized phenols	18.5%	16.4%	22.0%
Possibly lignin derived (<u>without</u> methoxyl groups) or microbially synthesized phenols	9.8%	17.8%	15.3%
Lignin derived phenols (<u>with</u> methoxyl groups)	Traces	2.3%	Traces
Unknown compounds	15%	19%	10%
Starting point	18%	19%	27.5%
Total recovery	62%	75%	85%

[1]   Activity in percent of the added material

      The numbers of phenols with methoxyl groups in experiments 1) and 3) are very low. This means that soil organic matter constituents in the garden soil did not participate in the synthesis of the newly formed humic acids during the six week incubation period. The degradation of lignin according to the experiments mentioned above (Grabbe and Haider, 1971) was relatively small during this time. Therefore, the percentage of microbially synthesized phenols may be relatively high in the section "lignin derived (without methoxyl groups) or microbially synthesized phenols". In the case of the addition of ^{14}C glucose, the low value in this column may be explained in this manner: the glucose was also used

as a source of energy for those micro-organisms which do not synthesize phenols in their metabolism, and was released as carbon dioxide. The addition of labelled straw increases the amount of possibly lignin derived phenols.

3.6 PARTICIPATION OF NITROGENOUS COMPOUNDS SUCH AS PROTEINS AND THEIR DEGRADATION PRODUCTS IN THE FORMATION OF HUMIC SUBSTANCES

The nitrogen content in soil organic matter is an important factor for soil productivity. The preponderant part of nitrogen is in the form of organic compounds and comes into the soil, for instance, by the addition of organic residual products, mostly from rural wastes, but also from municipal wastes, when the technical prerequisites exist. During humification processes the nitrogen is not linked in the form of nitrate or ammonium ions in soil organic matter, but only in the form of organic nitrogenous compounds or ammonia. The availability of this organically bound nitrogen for plant nutrition depends on the local conditions of microbial activity.

Experiments with ^{15}N labelled mineral nitrogen fertilizer have shown that approximately 50-60% of the nitrogen taken up in the harvested plant comes from the mineral nitrogen fertilizer and 40-50% from the nitrogen of soil organic matter.

Knowledge of the causal connections between nitrogen linkage in organic substances and its liberation from them for plant growth is very important for the economy of plant production. The nitrogen becomes available for the plant only by destruction of the carbon skeleton of the organic substances in the soils with all the unfavourable consequences for the mechanical properties of soils such as water holding capacity, soil erosion etc.

In the top 20 cm depth, soils contain between 2 000 and 9 000 kg N/ha. The question is: whether one should increase the decomposition of soil organic matter and use the liberated nitrogen for plant production, or not. According to present knowledge, one should try to keep a balance in soil organic matter by the addition of organic materials from different sources with additional doses of mineral nitrogen fertilizers when necessary. To obtain high yields per hectare an equalized humus husbandry is necessary. This fact has been neglected in many cases in developing countries in the last decades, whereas there was well regulated humus husbandry in former times, when organic materials were the only source of fertilizers.

The nitrogen content of humic acids as a fraction of soil organic matter is between 1-5% depending on environmental conditions during the formation. The distribution of nitrogen in humic acids was determined mostly by hydrolysis with 6 M HCl (Bremner, 1965). The types of linkage of the nitrogen in humic acids are as follows:

$$20 - 45\% \text{ as } \alpha\text{-}NH_2\text{-}N$$
$$10 - 25\% \text{ as } NH_3\text{-}N$$
$$1 - 5\% \text{ as } \text{amino-sugar-N}$$

At least 7-12% of α-NH_2-N is in the peptide bondings. About 50% of nitrogen remains in the residues of hydrolysis and is supposed to be bound to a large extent in heterocyclic form. The hydrolyzable nitrogen is the main source of available nitrogen for the nutrition of organisms in and on the soil. In this connection it may be remembered that humus can also serve as a slow release nitrogen fertilizer (Flaig and Söchtig, 1967).

The main reactions between different phenolic compounds and proteins, peptides or amino acids which may occur during humification are mentioned in Fig. 14.

Guajacol (I) and resorcinol (II) derivatives do not add amino acids in a pH-range of 6.5 to 8.0 in the presence of phenoloxidases in oxidizing medium. Guajacol derivatives react under these conditions to nitrogen free polymers (Flaig and Haider, 1961). The rate of nucleophilic addition or oxidative deamination depends upon the substitution of the phenols with hydroxyl groups in o-position (III). Both reactions generally occur simultaneously.
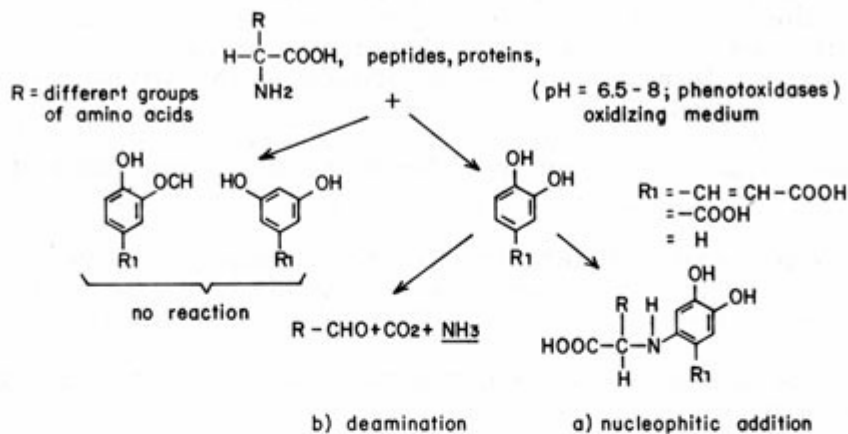
Fig. 13   Nucleophilic addition (a) of proteins and their degradation products by oxidized phenols; oxidative deamination (b) of amino acids

Extensive studies have been made with labelled amino acids about the possible linkage of proteins and amino acids during the nucleophilic addition (Haider, Frederick and Flaig, 1965). The hydrolysis of added products with proteins or peptides by 6 M hydrochloric acid has shown that all amino acids can be hydrolized with the exception of the N-terminal amino acid, in which the amino group has reacted with the oxidized phenol (Haider, Frederick and Flaig, 1965; Haider and Martin, 1970). Therefore, not all non-hydrolizable nitrogen is bound in humic substances in heterocyclic form, as is often supposed. This type of reaction is important in connection with the availability of organically bound nitrogen for micro-organisms and plants.

The amino acids are transformed into ammonia, carbon dioxide and into a carbonyl compound by oxidative deamination (Flaig and Riemer, 1971). The acceleration of the liberation of ammonia from amino acids by phenolic compounds under oxidizing conditions may be interesting in the processes of humification in relation to plant nutrition.

3.7   TECHNICAL PRODUCTS RESEMBLING SOIL ORGANIC MATTER USED AS SLOW RELEASE NITROGEN FERTILIZERS

It has been mentioned several times that nitrogenous constituents of soil organic matter serve as a slow release nitrogen source for plant nutrition. According to theory this nitrogen fertilizer should give the highest yield, providing nitrogen in sufficient amounts for the plant's needs during vegetation (Mitscherlich, 1948).

Some attempts have been made to prepare such a type of fertilizer by coating the granules with plastic or sulphur. Furthermore, nitrogen-containing compounds have been synthesized mostly by condensation of aliphatic aldehydes with urea or by oxidative ammonization of natural products such as peat, lignite or lignin containing waste products of the pulp and paper industry, such as lignin-sulphonates (N-lignin). The latter product can also be regarded as a contribution to environmental protection (Flaig, 1973).

Under certain conditions a favourable trend in yields, especially in the case of cereals, can be observed by the effect of slow release compared to mineral nitrogen fertilizer (Söchtig and Flaig, 1974). In addition, it can be demonstrated that the use of N-lignin inhibits the leaching of nitrogen by precipitation in different soils (Flaig and Söchtig, 1974).

Various problems in the field of slow release nitrogen fertilizer are still not yet solved, for instance: an improvement in the economy of synthesis for large scale use and investigation of the special effects on plant growth and yield under extreme climatic conditions. The oxidative ammonization of lignin or altered lignin (e.g. lignite) containing materials may be compared with a "humification" under very drastic reaction conditions.

3.8   MAIN REACTIONS DURING FORMATION OF HUMIC SUBSTANCES

The carbon content of the fraction of humic acids is about 0.2% of the dry weight of arable soils in temperate climates, or 20% of total soil carbon. The amounts differ widely according to the environmental conditions. Even this small amount of organic material is very important, mostly for the indirect effects on favourable plant growth.

Figure 14 represents the present day concepts on the formation of humic substances.

It has been mentioned several times already that phenolic compounds are important initial materials for the formation of humic substances. There are mainly two possibilities for their occurrence in soils:

i.   by stepwise degradation of lignin as a consequence of biochemical degradation;

ii.   by microbial synthesis from aliphatic precursors.

The high molecular weight molecule of lignin is degraded to smaller particles at first and finally to low molecular weight phenolic compounds. The phenol carboxylic acids can be isolated from soils. Quinonoid compounds, e.g. methoxy-p-benzoquinone, have not yet been isolated from soils, but this transformation was observed in plants (Harms et al., 1969 b). There is a report in a later section about the uptake of phenolic compounds by plants, their transformation and their effects on metabolism. During degradation of lignin cleavage of the aromatic ring also occurs and aliphatic compounds are formed. This part of lignin is lost for the formation of humic substances.

The phenols formed by microbial synthesis have mostly hydroxyl groups in m-position. They contribute to the synthesis of humic substances by nucleophilic addition to quinonoid intermediates of phenols with hydroxyl groups in o- or p-position. Phenols with hydroxyl groups in m-position add substances nucleo-philically only after hydroxylation in o-position to one of the existing hydroxyl groups. The participation of phenols of the resorcinol type in the formation of humic substances has been demonstrated by Haider and Martin (1967, 1968, 1970); Martin and Haider (1969, 1971); Martin, Richards and Haider (1967).

Fig. 14   Formation of humic substances

(SCHNITZER 1965) Elementary analysis					Functional groups meq/g				N — distribution in % of total N			
Podzol B	% C	% H	% O (Diff.)	% N	COOH	—OH (phenol.)	—OH (alcohol)	>C=O	Hydrolysate			Residue N
									α-NH₂-N	NH₃N	Glucos-omine-N	
Humic acids	56.72	5.21	35.35	2.37	1.5	4.2	2.7	0.9	20-40	10-25	5	~50%
Fulvic acids	50.92	3.34	44.74	0.74	9.1	3.3	2.6	3.1				

Formation of complexes with ions of heavy metals and inorganic soil constituents
Polydispersed systems of higher molecular, structureless polyanions

The dark coloured humic substances are formed in an oxidizing medium by random-polymeridation of oxidizable phenols with protein, peptides, amino acids and their degradation products. According to their solubility in alkaline and acid solutions the humic substances are separated by conventional methods in the fractions fulvic acids, humic acids and humins.

The manifold possibilities of reactions explain the three dimensional poly-condensation by which the high molecular weight, polidispersed, cross-linked humic acids are formed. According to Schnitzer (Ogner and Schnitzer, 1971; Khan and Schnitzer, 1971) one can estimate in which way the different phenolic constituents are connected by carbon-carbon linkages.

Fractions of humic substances have been exhaustively methylated and oxidized afterwards with potassium permanganate; the esters of different benzene polycarboxylic acids were identified. The carboxyl groups can belong to a linkage of an aliphatic side chain with an aromatic ring or between two aromatic rings.

The carboxylic and phenolic groups cause the acid nature of the humic acids and participate in complex formations with heavy metals and inorganic soil constituents. In one of the next paragraphs interactions with high molecular weight polymers will be mentioned.

3,4-dimethoxybenzoic-acid methyl ester

3,4,5-trimethoxybenzoic-acid methyl ester

4,5-dimethoxy-1,3-benzene-dicarboxylic (isohemipinic) acid dimethyl ester

3-methoxy-1,2-benzenedicarboxylic

4-methoxy-1,3-benzene-dicarboxylic

acid dimethyl ester

3,4-dimethoxy-1,2-benzenedicarboxylic (hemipinic)

3-methoxy-1,2,4-benzenetricarboxylic acid trimethyl ester

5-methoxy-1,2,3,4-benzenetetracarboxylic acid tetramethyl ester

4,5-dimethoxy-1,2-benzenedicarboxylic (metahemipinic) acid dimethyl ester

5-methoxy-1,2,4-benzenetricarboxylic acid trimethyl ester

4-methoxy-1,2,3-benzenetricarboxylic acid trimethyl ester

methoxybenzenepentacarboxylic acid pentamethyl ester

2-methoxy-1,3,4,5-benzenetetracarboxylic acid tetramethyl ester

Fig. 15   Isolation of phenolic acids after methylation and oxidation
(Ogner and Schnitzer, 1971; Khan and Schnitzer, 1971)

According to the functions of nitrogen in the humic fractions, its availability for organisms varies. The hydrolyzable part is more available than residual nitrogen, a form which one supposes is mainly in heterocyclic compounds.

The total nitrogen content of humic acids isolated from soils is, on average, 2-4%. This is from humic acid-like products synthesized by micro-organisms in culture solutions of about 7%, from which 50% can be determined as α-amino-nitrogen.

The longer the chain length of the peptides, the more α-amino-nitrogen is recovered by hydrolysis or the more carbon dioxide is evolved by microbial activity, whereby also phenolic components are degraded (Martin et al., 1975). This fact can be concluded from the different amounts of carbon dioxide evolution from the humic acid-like polymers synthesized by Stachybotrys atra before and after hydrolysis as well as by "model humic acids" formed in an oxidative medium from

phenolic compounds in the absence or presence of peptone. The experiments were carried out in a sandy loam under standard conditions. For comparison, the values of carbon dioxide evolution in the case of corn stalks, peat humic acids and for the soil alone are given.

Table 6   DECOMPOSITION OF SOME MODEL AND NATURAL HUMIC ACID-TYPE POLYMERS IN GREENFIELD SANDY LOAM
(Martin et al., 1975)

Polymer source	Percentage decomposition[1] after weeks:					
	1	2	3	4	6	8
Soil	0	0	0	1	1	1
Stachybotrys atra	5	7	9	9	11	12
S. atra hydrolyzed	1	1	1	1	1	2
Aspergillus sydowi	5	7	9	9	11	12
Epicoccum nigrum	1	3	4	5	7	9
Hendersonula toruloidea	4	5	5	5	6	6
Autoxidative model "humic acids" incorporating phenolic compounds only	0	0	0	1	1	1
" phenols and peptone	1	2	3	4	5	6
Peat (Leonardite)	1	2	3	4	5	5
Corn stalks	29	50	54	56	59	61

1/ Percent of added carbon evolved as CO_2.

The mean time of residence of humic substances in soil is much longer than that of the initial material (Sauerbeck and Führ, 1968). This is one of the reasons why fractions of soil organic matter are important for soil conditioning. This subject will be treated later in Chapter 4.

3.9   THE INFLUENCE OF MINERAL SOIL CONSTITUENTS ON THE BIOCHEMISTRY OF SOIL ORGANIC MATTER

It was mentioned before that the amount of available nutrients, chiefly nitrogen, and the existing climatic factors influence not only the rate of transformation of organic materials in soil during humification but also the composition of the newly formed substances. Different authors describe that clay minerals exert a pronounced influence on soil ecology and that it is mainly the surface active clay minerals, such as montmorillonite, which have a greater effect than kaolinite and quartz (summarized in Filip et al., 1971 a).

In relation to the microbial synthesis of humic acids, experiments in stationary or in shake cultures of Epicoccum nigrum and Stachybotrys chartarum have shown that the addition of montmorillonite in a small concentration accelerates the formation of humic acid-type polymers and in some cases also increases their amount in culture solution (Filip et al., 1971 b). The humic polymers formed had almost the same properties whether clay minerals were present or not. The percentage of nitrogen and carbon, the total acidity, content of carboxylic groups and the exchange capacity did not alter. The structure and relative amount of phenols after reductive cleavage with sodium amalgam of the phenols were the same in both cases as mentioned previously. The formation of phenols in cultures with montmorillonite was only accelerated, not changed. Furthermore, the interesting observation has been made that the same effects on the formation of humic acid-like polymers occur when montmorillonite is enclosed in a dialysis tube.

There is some evidence that the alterations in the processes described are connected with some sorption phenomena of the low molecular weight substances on the clay minerals. In these experiments, and in some others, it was demonstrated that biomass production, glucose consumption, nitrogen assimilation and the formation of metabolic intermediates are generally enhanced (Filip and Haider, 1971 c; Haider et al., 1970; Bondietti et al., 1971).

The clay minerals have a common importance for the biochemistry of soil organic matter. The main transformations of organic materials in soils are caused by the intra- and extracellular enzyme systems especially from micro-organisms. Very recently McLaren (1975) published a review of these problems.

During degradation of organic materials added to the soil, as well as coming from the exudates of plants and micro-organisms, a large number of different organic compounds develop in the soil but no enrichment with special compounds can be observed in time. Depending on the local conditions, a dynamic balance exists. Therefore, the soil would appear to contain all the enzymes which catalyse the reactions of decomposition. Some of them have been demonstrated in soil.[1] Because most of the enzymes cannot be isolated in a pure state, they must have interacted with clay minerals or fractions of the humic system. They do not lose their activity by these interactions (compare: Thornton et al., 1975). When microbial activities are altered by mechanical treatments or by the addition of chemical compounds such as mineral fertilizers, the catalysis by enzymes of the reactions occurring from the transformation of organic substances is influenced. This fact must be borne in mind if organic materials are used as fertilizers.

3.10 ORGANIC COMPOUNDS IN SOIL

The organic compounds in soil are usually derived from living or dead organisms in and on soils, such as plants, animals and micro-organisms. Some more substances are formed by biochemical reaction which are not present in the original organisms; their amounts in soils vary and the quantity depends on the existing environmental conditions. In cultivated soils, however, small amounts of organic agrochemicals such as pesticides and their degradation products are found, also other organic compounds which derive from waste disposal, mainly from municipal rather than from rural waste materials. There are several reviews and literature available on this subject.[2] Not all compounds will be mentioned in detail, attention will be given to a few.

The content of aliphatic acids is between 0.1 - 0.9 meq/100 g soil. The level of amino acids does not exceed 2μ/g soil. The largest part of amino acids is bound in proteins or sorptively on other soil constituents.

The sugars are mainly bound in the form of polysaccharides. About 6-16% of soil organic matter consists of carbohydrates. Some of the poly saccharides are linear polymers and influence remarkably the soil structure (see Chapter 4). Organic phosphorus compounds occur in the form of nucleic acids and their components, or in the form of inositol phosphates.

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[1] Durand, 1965; Hofmann and Hoffman, 1966; Voets and Dedeken, 1966; Skujins, 1967; Kuprevich and Shcherbakova, 1971; Galstian, 1974; Rotini and Sequi, 1974.

[2] e.g. Flaig, 1971; Greenland and Oades, 1975; Parsons and Tinsley, 1975; Anderson, 1975 a, b; Braids and Miller, 1975; and the annotated publications of "Soils and Fertilizers" and others.

Apart from phenolic compounds, the formation of which was discussed above, some compounds can be derived from phenolic plant constituents such as flavanones, flavanoles, catechines and others (e.g. Bate-Smith and Lerner, 1954; Coulson et al., 1960). The amount of phenols, derivable from lignin, decreases with the depth of the soil profile (Bruckert et al., 1967 and others). Whitehead (1964), for instance, determined the concentration of different phenolcarboxylic acids in surface soils and reported their contents as about 10^{-5} mol/litre or 10 ppm. Similar investigations were made by Guenzi and McCalla (1971). In alkaline extracts of peat the concentration of phenolcarboxylic acids varies between 10 and 1 000 ppm (Söchtig and Maciak, 1971). The importance of phenolic compounds for a favourable effect of soil humus on plant growth is not yet completely understood, not even after numerous investigations in sand and water cultures, in field experiments or by special investigations of plant metabolism (summary: Flaig, 1968).

In soils, other phenolic or quinoid compounds are found such as 3-nethyl-1, 4-naphthoquinone (Mathur, 1971), 2-methoxy-1,4-naphthoquinone (Lambert, 1971) or anthraquinones (Kumada and Suzuki, 1967). McGrath (1972) isolated different hydroxy-anthraquinone derivatives.

Chrysophanol   Chrysotalunin
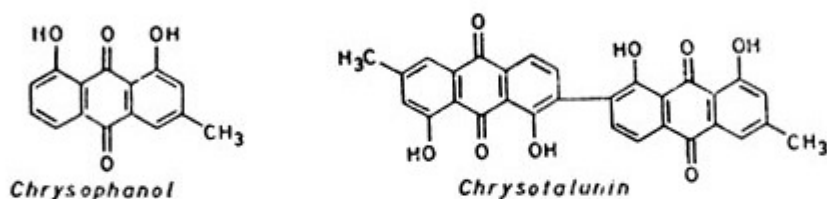
Chrysotalunin occasionally amounted to more than 120 ppm of soil, whereas the other compounds were less than 4 ppb. Furthermore it could be demonstrated that special soil micro-organisms, e.g. Eurotium chinolatum, synthesize anthra-quinones (Saiz-Jimenez et al., 1975). These observations may be interesting in relation to plant growth, because anthraquinones increase the length of roots of Lepididium sativum in culture solutions (Flaig and Otto, 1951).

Benzo(a)pyrene

Another group of compounds - polycyclic aromatic hydrocarbons (PAH) - will be mentioned in connection with the use of municipal waste as organic fertilizers (Chapter 5). Their oxidation products, e.g. benzo(a)pyren, are cancerogenic. These types of compounds were identified after reduction of humic acids with zinc dust (Cheshire et al., 1967) or were isolated in small amounts from soils (Blumer, 1961). More data are given in Chapter 5 (compare the list of other polycyclic compounds in Braids and Miller, 1975, pp. 346-348).

3.11   UPTAKE, TRANSPORT AND TRANSFORMATION OF PHENOL CARBOXYLIC ACIDS (LIGNIN DEGRADATION PRODUCTS) IN PLANTS

In section 3.3 it was mentioned that one of the direct effects of constituents of humus on plant growth may be the uptake of compounds by the roots of plants and their influence on metabolism (see also section 4.8). Therefore the uptake, the

transport and the transformations of phenolic lignin degradation products, such as p-benzoic, vanillic and syringic acid by plants, were studied (Harms, 1968; Harms et al., 1969 a, b, 1971).

For this purpose the phenol carboxylic acids were labelled at different carbon atoms such as at the carboxyl group, the carbon atom of the methoxyl group or uniformly in the benzene ring and added to the nutrient solution of sterile cultivated wheat seedlings in a special experimental set. The plants were prepared by lyophylization for extraction. The activity of the residues of extraction with different solvents was determined. In this way statements could be made about the fixation of the activity in the course of reactions occurring and in different plant constituents. As an example of such experiments the results of the addition of ^{14}C-carboxyl-labelled vanillic acid are cited (Harms et al., 1969 b).
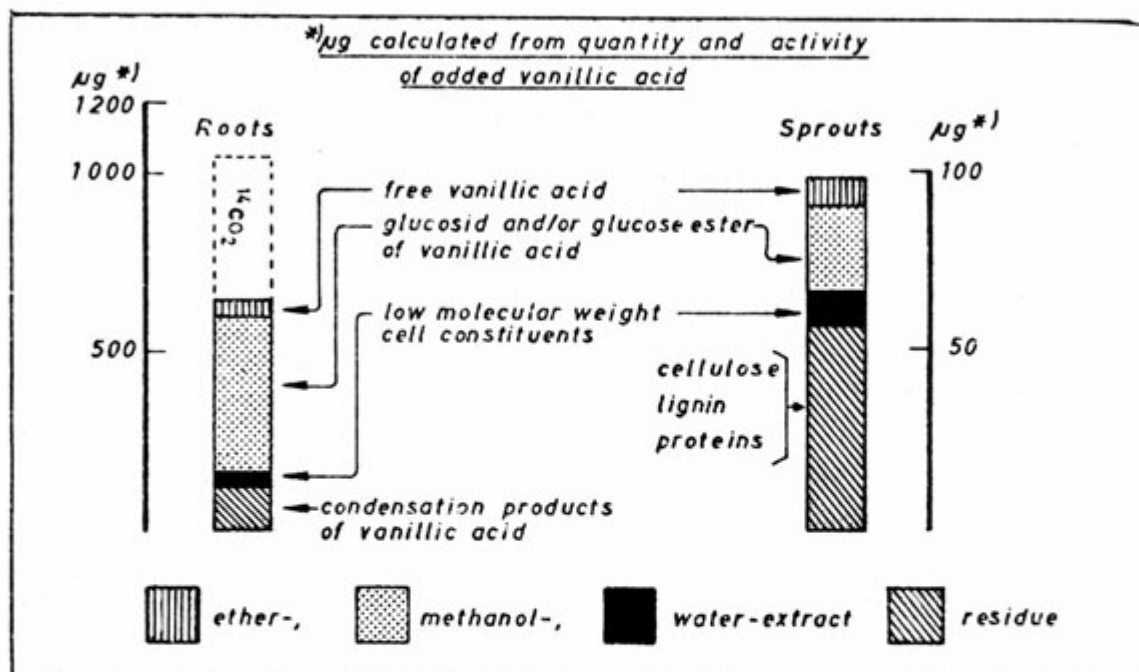
Fig. 16 Content of activity in the extracts of roots and sprouts after incubation with carboxyl-labelled vanillic acid for 6 days (Harms et al., 1971)

The main results are:

- the accumulation of activity in the roots is about 10 times higher than in the sprouts;

- the quantity of free vanillic acid in the plant is relatively low according to the radioactivity of the residues in the ether extracts;

- the largest part of activity was in the methanol extracts. By further investigations it was found that vanillic acid is transformed into glycosides, in glucose ester or into glycosides of glucose ester;

- in the water extracts some ^{14}C-labelled plant constituents could be identified;

- in the residues of water extracts of the sprouts, cellulose, lignin and proteins contained radioactivity by endogenous fixation of labelled carbon dioxide, which was formed by oxidative decarboxylation of the added ^{14}C-vanillic acid;

- the activity in the residues of water extracts of the roots was caused by oxidative polymerization of vanillic acid together with some degradation products;

- the relatively high release of labelled carbon dioxide is a measure of the oxidative decarboxylation of vanillic acid. By this reaction methoxy-hydroquinone is formed and could be identified in a quantity corresponding to about 1% of the added activity.

These results are interesting because hydroquinones are 10 to 100 times more physiologically active in plant metabolism than the corresponding phenol carboxylic acids. Furthermore, particular reactions of phenol acrylic or carboxylic acids have been studied in cell suspension cultures, especially the O-demethylation (Berlin et al., 1971, Harms, 1972; Harms et al., 1972).

The studies on the uptake of phenol carboxylic acids by plants may be interesting in so far as observations exist that some varieties of cereals are the more resistant to Fusarium and other fungal diseases the higher the content of phenolic compounds, which are identical to those mentioned. Moreover, some investigations have been published about higher resistance by potatoes to Phytophtera if there is a higher content of phenolic substances in the plant (Olteanu and Brad, 1969). More research work should be done to clarify the biochemistry of these processes, because they are interesting for increasing the natural resistance to diseases and, therefore, are a remarkable contribution to environmental protection by diminishing the use of often not-so-harmless fungicides. In connection with such investigations, more attention should be paid to the possible contributions of soil organic matter. The phenolic compounds mentioned can be isolated from soils.

3.12 INFLUENCE OF PHENOLIC COMPOUNDS ON ENZYMES IN SOIL

Hydroquinones or the corresponding quinones inhibit nitrification and urea activity (Bundy and Bremner, 1973, 1974, also Flaig and Söchtig, 1967). The effect of these quinones on the inhibition of nitrification is comparable to that of commercial chemicals.

50 µg substance/g soil, 30°C, 50% max. water capacity, incubation time 14 days
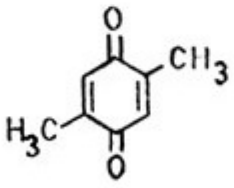
p-benzochinone	Inhibition of urea activity	Inhibition of nitrification
2,3-Dimethyl-	80%	39%
2,5- "	82%	70%
2,6- "	79%	69%
compare: N-Serve, Down Chemical, USA 2-Chloro-6-(trichloromethyl)-pyridine		80%
AM, Toyo Koatsu Industries, Japan 2-Amino-4-chloro-6-methyl-pyrimidine		31%
ST, Sigma Chemical Co., USA Sulphathiazole		22%

Fig. 17   Inhibition of urea activity and nitrification by quinones (Bundy and Bremner, 1973, 1974)

The consumption of urea as a fertilizer is increasing steadily because of its high nitrogen content of about 46% (Bremner and Hauck, 1974).

Over-high concentrations of ammonia, with its toxic effect on young plants under special climatic conditions, can be avoided by using inhibitors of urea activity. The inhibition of nitrification diminishes the leaching of nitrate into the deeper horizons of the soil by rainfall. Nitrification is also inhibited by the low molecular weight fraction of the slow release nitrogen fertilizer N-Lignin. According to model experiments the effect may be caused by the degradation products of oxidized lignin.

Biochemical studies of soil organic matter, and its constituents, explain some of its favourable effects on plant growth and yield, which cannot be caused by improvement of physical conditions in soils or by additional fertilization with inorganic nutrients (Flaig and Söchtig, 1973).

4. IMPORTANCE OF SOIL ORGANIC MATTER TO SOIL FERTILITY

4.1 SOIL ORGANIC MATTER AS A SOURCE OF PLANT NUTRIENTS ESPECIALLY NITROGEN

Organic matter plays an important role in the life processes in the soil and a brief description of its significant role in plant nutrition is given here.

The plant is composed mainly of organic compounds, containing carbon, hydrogen and oxygen and, to a lesser extent, nitrogen. The first three elements are taken up by plants as carbon dioxide and water which are final products of the decomposition of the soil organic matter, but experiments show that only traces of this carbon dioxide can enter the plant through the root system (Kick et al., 1965; Sauerbeck and Führ, 1966). Most of the carbon dioxide from the decomposition of soil organic matter is released into the atmosphere and enters into the common cycle. In dense vegetable formation, e.g. potatoes or beets, this carbon dioxide can be stored near the soil surface and used by plants via the leaves.

A direct uptake of low molecular organic compounds is observed mostly in water cultures under more or less sterile conditions, but the same should be possible in soil.

The uptake of amino acids through the roots has been proved by Virtanen (1935), Virtanen and Linkola (1946) and Mietinen (1963). Some of the amino acids under investigation in these experiments showed a specific influence on plant growth. How far the uptake and direct metabolization of amino acids in plants contribute to yield production under field conditions is not yet known.

Winter et al. (1959 a, b) demonstrated qualitatively the uptake of phenolic compounds by bean and wheat plants as well as arbutine, phlorozine and other compounds. The phenols were transformed to glucosides in the wheat plant (Winter, 1960). Phenolic compounds, also isolated from soils, can be taken up through the roots, but only traces are transported to the sprouts, partly oxidized to quiononoid compounds; the main part is immobilized in the form of glucosides and/or their glucose esters. [1]

On the contrary it does not seem possible for plants to take up humic substances. Prat (1963 a, b) observed that the dark-coloured humic substances extracted from soil cannot diffuse through an onion epidermis used as a membrane for dialysis and do not appear in guttation drops. If the cut sprouts are put in a solution of the same humic substances, the dark-coloured compounds can diffuse only slowly over a short distance and are quickly coagulated in the cell soap. Führ and Sauerbeck (1967) also observed that ^{14}C-labelled humic acid fractions of rotted straw do not pass the epidermis of a carrot. Only traces of them were taken up by sunflower roots (Führ and Sauerbeck, 1966).

The soil organic matter is the main natural source of nitrogens; only small amounts can be fixed by micro-organisms from the air or can enter the soil via rainfall. The content of humus and nitrogen is described in the main soil types of the USSR (Kononova, 1975).

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[1] Söchtig et al., 1968; Harms et al., 1969 a, b; 1971; Kastori et al., 1970 = Sdd Nr. 235, 251, 254, 273, 265.
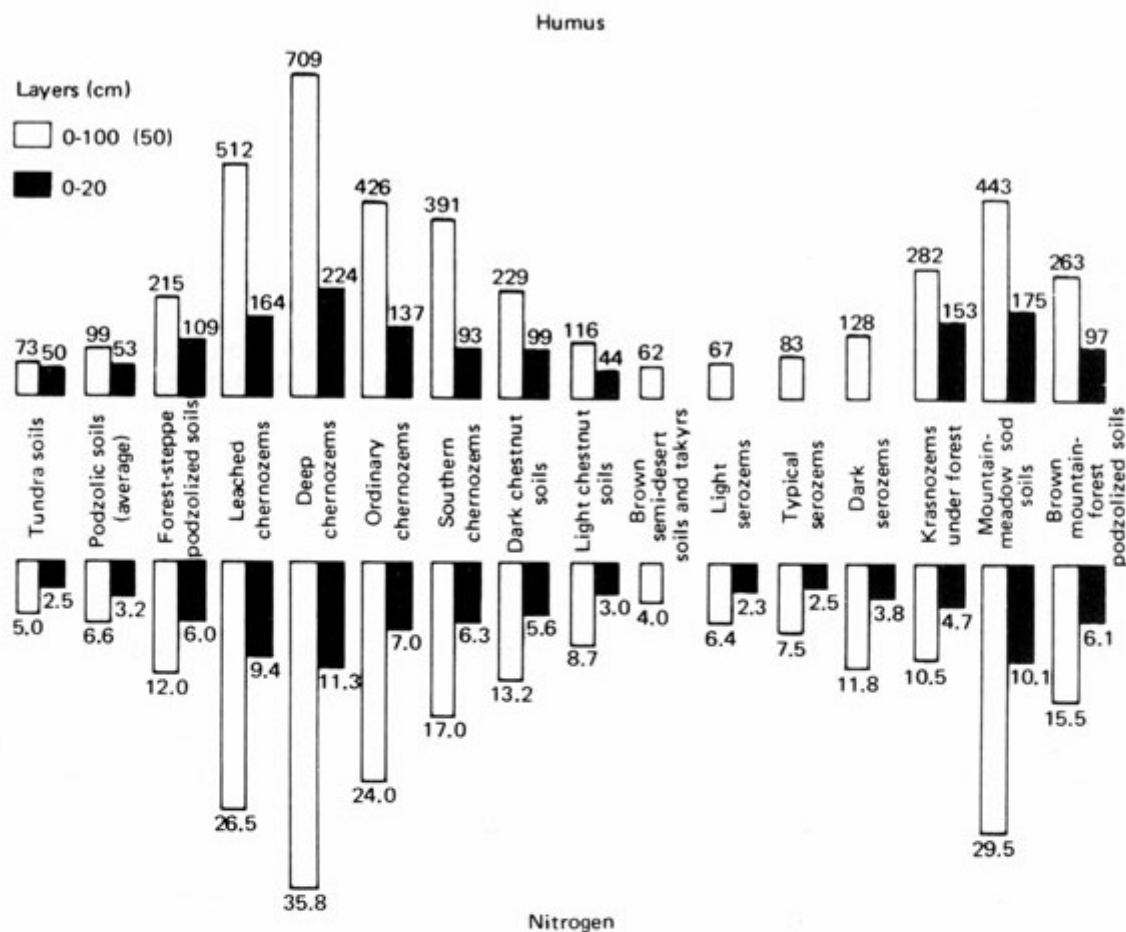
Fig. 18   Humus and nitrogen content (tons/ha) of soil
            columns of different lengths (Kononova, 1975)

The nitrogen content in a soil increases with its amount of humus. On average about 2 300 - 11 300 kg nitrogen/ha are stored in the upper layer (0-20 cm) of a mineral soil and about 4 000 - 35 800 in the 0-100 cm layer. The percentage contents of soil organic matter and nitrogen decrease with the depth of the profile, depending on the soil type.

Broadbent (1968) described the dynamic equilibrium between inorganic and organic nitrogen in soil and the control of the availability of nitrogen to plants and micro-organism by the two opposite processes - immobilization and mineralization. Immobilization decreases the availability of nitrogen by fixation of ammonium ions within the layers of clay minerals, by assimilation by micro-organisms and fixation in their organic nitrogenous compounds and liberation in the form of ammonia. This process depends largely upon the activity of micro-organisms. Jansson (1958) postulated a large pool of passive organic nitrogen supplying very little to available nitrogen. Scarsbrook (1965) reports that 2-4% of the nitrogen in soil organic matter is mineralized per year.

4.1.1 Effect of Soil Factors on Nitrogen Immobilization

Broadbent (1968) considered the fixation of ammonium by clay minerals as an irreversible component of immobilization and describes that tagged nitrogen applied in the form of ammonium sulphate to a Columbia fine sandy soil containing a small quantity of vermiculite is fixed to a distinct amount in some hours without further changes within the time of the experiment, whereas the exchangeable nitrogen disappears slowly within 15 days. The immobilization of ammonia reacting with soil organic matter (fixation of ammonia by soil organic matter) was studied by Mattson et al. (1942) and reviewed by Shortland and Walcott (1965). The results of this type of experiment show that soil organic matter fixes a larger quantity of ammonia than the clay. Its availability to the plant seems to be very low (Burge and Broadbent, 1961).

The biological immobilization depends largely upon the conditions influencing the activity of micro-organisms. In the initial phase, within two weeks or less, a very rapid decrease of inorganic nitrogen occurs, followed by a period of mineralization, but the initially fixed nitrogen seems to be quite stable. A number of soil factors affect the rate of the turnover.

The influence of temperature on immobilization shows that maximum immobilization is reached in a shorter time with increasing temperature, but the amount of immobilized nitrogen is not significantly affected. These results were found after addition of 100 ppm N in the form of tagged ammonium sulphate. The mineralization of the immobilized tagged nitrogen is slower than that of the initial soil nitrogen (Broadbent, 1968). The effect of the source of nitrogen is shown by Jansson et al. in three different soils after adding 100 ppm N as tagged ammonium sulphate or tagged calcium nitrate with 1% oat straw by determination of the tagged nitrogen in the organic fraction. Even though the ammonium is very quickly nitrified, the nitrogen of the ammonium sulphate is immobilized much more rapidly and to a higher amount. But the immobilized ammonium nitrogen seems to be remineralizable, whereas the immobilized nitrate remains in this state during the 60 days of the experiment.

With increasing soil pH, the immobilization of ammonium nitrogen increases, that of nitrate decreases, without and with straw, but the effect of pH is more pronounced after the addition of straw.

4.1.2 Chemical Nature of Immobilized Nitrogen

It can be assumed that the immobilization of nitrogen by micro-organism activity results in an increase in tagged nitrogen in the fraction of amino acids. Analysis of hydrolysates confirms this fact.

The tagged N-content is larger than in hexoseamine, amino acids and in other hydrolyzable nitrogen, but smaller than in amide nitrogen and non-hydrolyzable nitrogen. After 454 days only small differences in the distribution of nitrogen were observed but these small differences suggest that some of the amino acid nitrogen can be converted into other forms, possibly more resistant to biological attack.

4.1.3 Plant Recovery of Immobilized Nitrogen and Other Elements

Broadbent (1968) shows a very small recovery of previously immobilized tagged nitrogen by pot experiments with grass. Only the first cut, and to a lesser extent the second cut assimilated mineralized tagged nitrogen. Bartholomew (1965) in his review also came to the conclusion that the nitrogen added as organic material and not mineralized in the first year becomes a part of the soil organic matter and decomposes slowly over a period of many years.

Furthermore, the mathematical calculations of Broadbent (1968), based on the results of Woodruff (1949) and the constants calculated by Bartholomew and Kirkham (1960), show a very small rate of turnover of immobilized nitrogen. Reviews of nitrogen forms in soil and of methods to determine the different forms of nitrogen in soil are given by Bremner (1965, 1968) and Parsons and Tinsley (1955).

Phosphorus and sulphur are taken up by plants mainly in the form of inorganic anions as phosphate and sulphate. The organic compounds of phosphorus (Anderson, 1975 a) and sulphur (Anderson, 1975 b) contribute to the nutrition of plants depending on their decomposibility and the activity of micro-organisms.

4.2   CONTRIBUTION OF SOIL ORGANIC MATTER TO SOIL CONDITIONS

Soil structure is a result of the interactions mainly between inorganic soil colloids such as clay minerals or sesquioxidehydrates, polyvalent cations, and fractions of soil organic matter. Favourable or unfavourable effects of the soil structure depend on soil climatic factors as they condition chemical reactions and microbial activities, on chemical composition and on physical properties of the inorganic soil colloids as well as the properties of fractions of soil organic matter, which are caused by their chemical structure.

According to numerous investigations, it is mainly the high molecular weight fractions of humic substances that participate in interactions that form the soil structure (Flaig et al., 1975) and are important factors effecting soil conditions.

Regarding the scheme of the principles of formation of humic substances in general (Chapter 3), the following diagram illustrates the formation of the main organic polymers in soil.
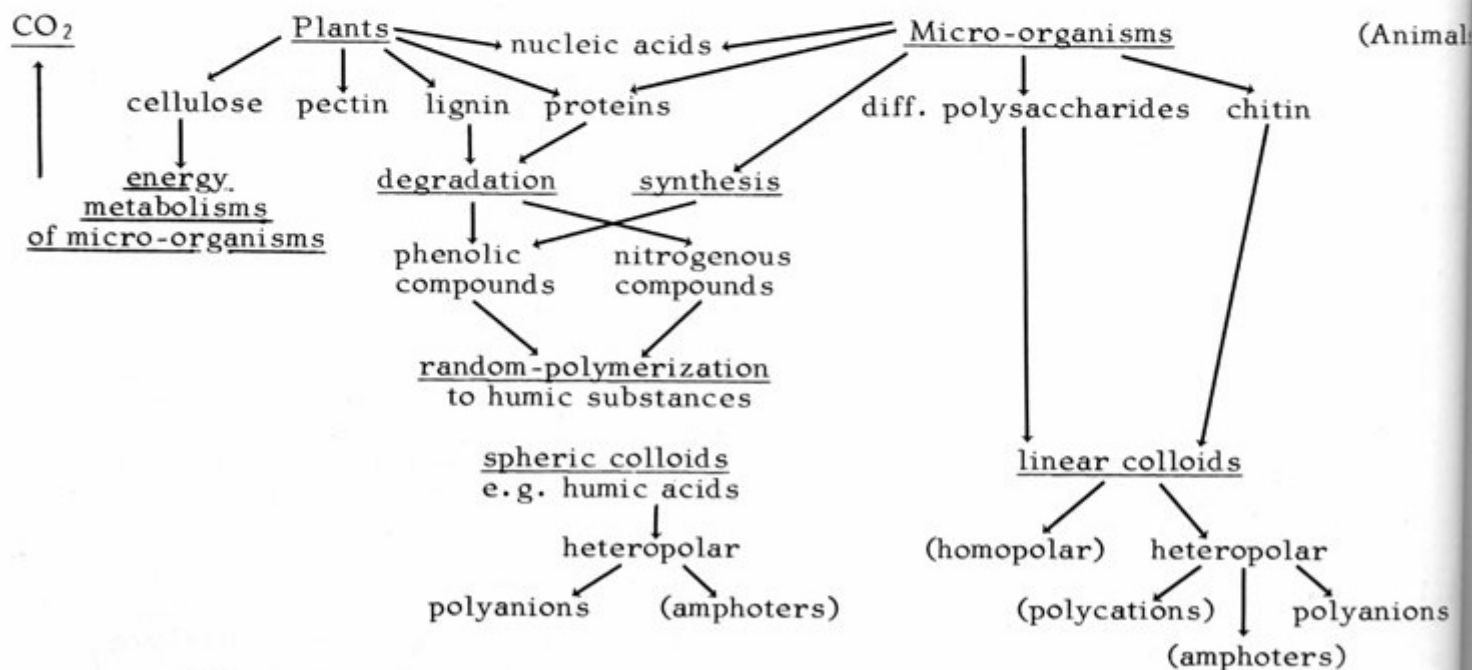
Fig. 19   Transformations of high molecular weight, main constituents of organisms in spheric and linear polymeric fractions of soil organic matter

The main organic, high molecular weight constituents of plants are cellulose, pectin, lignin, proteins and, to a smaller amount, nucleic acids. From them: cellulose is used in the energy metabolism of soil micro-organisms and released to a large part in the form of carbon dioxide as a metabolite; and plant pectins are more or less easily decomposed by the activity of micro-organisms. Besides protein and nucleic acids, the micro-organisms contain chitin and synthesize different polysaccharides according to their species.

Animals contribute little to high molecular weight fractions of soil organic matter because most of their high molecular body substances are utilized by micro-organisms for their metabolism.

One of the most important building blocks of humic substances is that of the phenolic compounds as mentioned previously. These occur in soil by degradation of lignin or by synthesis in the metabolism of micro-organisms from aliphatic precursors. By random-polymerization with nitrogenous degradation products of proteins, the formation of the different fractions of humic substances occurs. The humic acids are spheric colloids with the properties of heteropolar polyanions and, to a lesser degree, amphoters (Chapter 3).

The chitin and the different polysaccharides, formed in the metabolism of soil micro-organisms, are linear colloids. Most of them are heteropolar anions. Some of them may have the properties of amphoters, when for instance glucosamine is a constituent of the high molecular chain. The presence of high molecular weight polycations in soils can be excluded in all probability.

Besides the high molecular weight substances, filamentous material such as hyphae of fungi, small root hairs, etc., also plays an important role in the formation of soil fabric. But in relation to biochemistry of soil organic matter only the contributions of the mentioned polymers will be discussed.

4.2.1   Effect of Polymers in Relation to Soil Fabric

i.   Spherical soil colloids (humic acids)

In the arable soils of the temperate climate about 0.2% of their weight is the carbon fraction of humic acids; their importance for different physical properties has already been described. By physico-chemical measurement it has been demonstrated that humic acids consist of heteropolar globular-shaped particles with a negative charge. They form micelles which increase in size with increasing hydrogen ion concentration (summaries in: Flaig et al., 1975).

Aggregation and dispersion of humic acids, as influenced by pH values, can be followed in principle with the electron microscope (Beutelspacher, 1955a, b) (Fig. 20). In an alkaline medium (pH = 8) the humic acids are dispersed in almost single particles, whilst in an acidic (pH = 3.5) medium aggregates are formed. The negative charge of humic acids is caused by the acidic carboxyl and phenolic hydroxyl groups. Through investigations with model substances one can assume that amine groups are also present in humic acids, which could contribute to some amphoteric properties.

With increasing nitrogen content the sponge-like particles become more compact and less hydrated (Flaig and Beutelspacher, 1954; Orlov and Groskova, 1965). The copolymerization of nitrogenous compounds may also cause a connection between phenolic compounds and the formation of heterocyclic ring compounds. The latter are mostly less degradable by micro-organisms than nitrogen compounds with an aliphatic chain connected with aromatic rings. The functions of the nitrogen in the humic acids also determine the rate of decomposition and the function of the slow release nitrogen source.
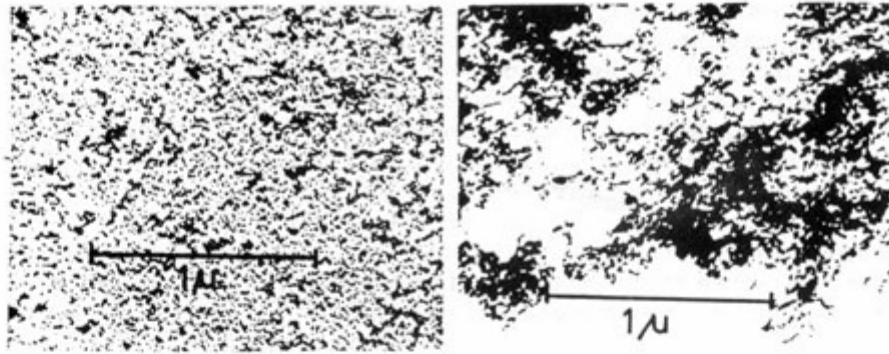
Fig. 20   Humic acids (pH = 8 and 3.5) (electron microscope)
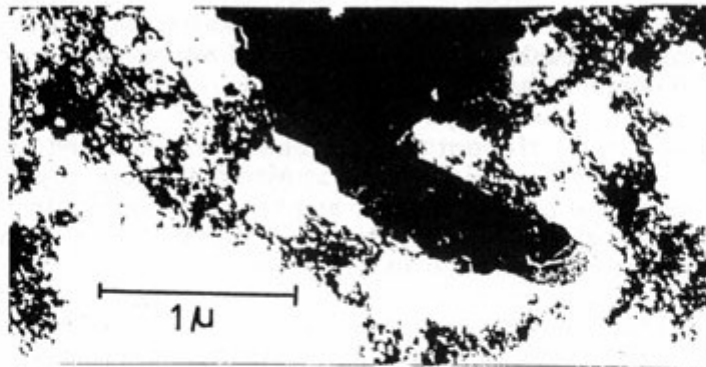
Fig. 21   Electrodialized kaolinite and humic acids isolated from
                 chernozem at pH = 6   (electron microscope)

Fig. 22   Interactions between "krilium" and kaolinite
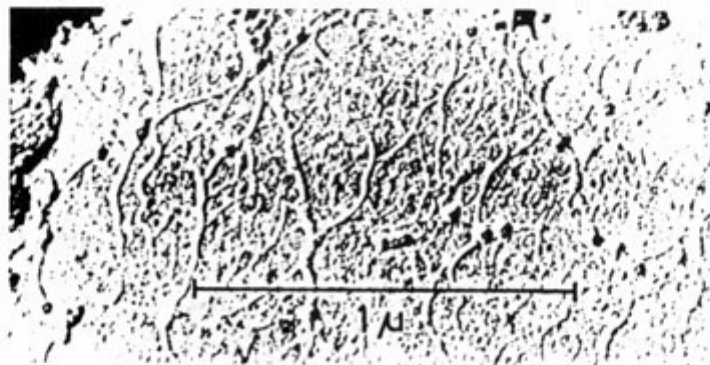
Fig. 23   Filamentous particles in earth worm castings
                 (Beutelspacher, 1955)   (electron microscope)

The interactions between the inorganic and organic soil colloids are an important factor for the stabilization of the aggregates and therefore for soil productivity (Theng, 1974). In these processes the polycations (such as of calcium and sesquioxidehydrates mainly from iron and aluminium) as well as colloidal silicic acid play an important role in these reactions.

If electrodialized, the humic acids and kaolinite are negatively charged colloids and no interactions occur (Fig. 21). The shadowing with platinum shows that an oriented sorption occurs neither at the edges nor on the surface of the crystals. An interaction can only be observed when the charge of the surface of kaolinite is changed by sorption of sesquioxidehydrates of aluminium and iron or by polyvalent cations. Such observations have been made by many other authors.

Recently Valla, Guckert and Jacquin (1972 a, b) investigated the formation of complexes between $C14$-labelled humic acids and montmorillonite loaded with different ions. They found that the adsorbed amount of humic acids per surface decreases in the row with Fe^{+++}-, H^{+}- and Ca^{++}-montmorillonites. They made the observations by extraction with the classical solvents, sodium hydroxide or pyrophosphate, that the complexes with Ca^{++}-montmorillonite are more stable than those with H^{+}-montmorillonite and these again more than those with Fe^{+++}-montmorillonite. The process of complex formation with triple layer clay minerals is much stronger than with double layer clay minerlas.

ii.   <u>Linear soil colloids (polysaccharides and linear polyelectrolytes as model substances</u>

The other types of more or less high molecular weight substances in soil are linear colloids, mainly the microbially synthesized polysaccharides.
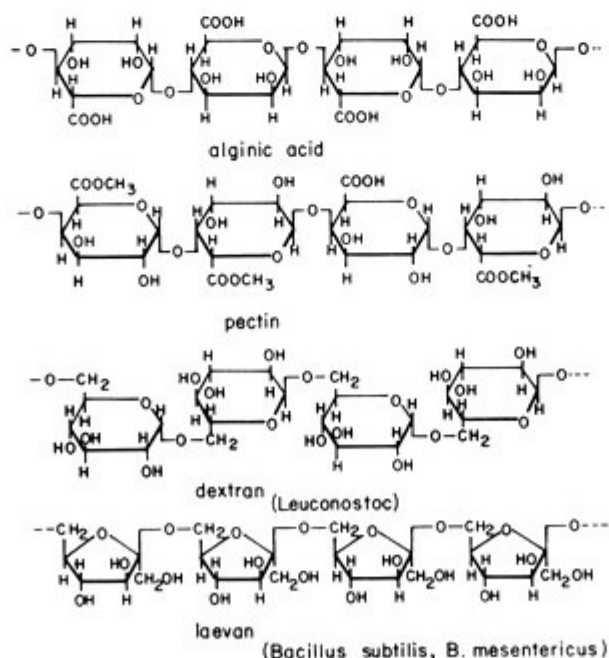
Fig. 24   Natural linear colloids

In contrast to humic acids they consist of a smaller number of monometers. The microbially synthesized polysaccharides in culture solution are formed by three different monomers on the average. In the polysaccharides fractions isolated from soils about 10 different monomers have been identified by hydrolysis. It is estimated that 5-20% of the organic substances present in soil are polysaccharides. As mentioned, they are mostly polyanions and are water soluble or dispersible. The influence on aggregation of inorganic constituents is very strong. As an example the classical work of Rennie, Truog and Allen (1954) in this field is cited.
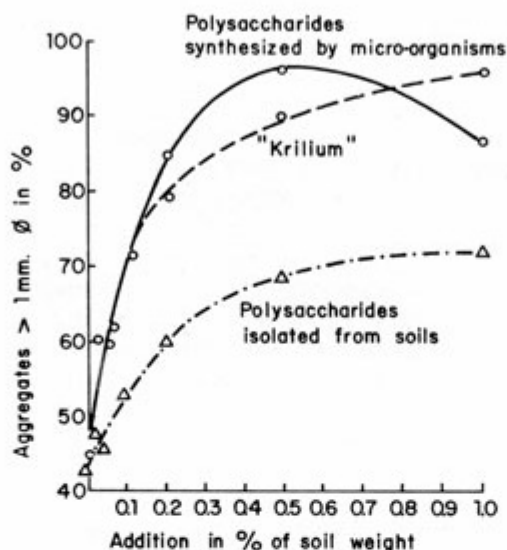
Fig. 25   Effect of different linear polymers on crumb formation
                    (Rennie, Truog and Allen, 1954)

The effect on formation of soil aggregates is stronger in the case of microbially synthesized polysaccharides than in the case of poly-saccharides isolated from soils. This may depend upon the chain length of soil polysaccharides. The strong effect on the formation of stable soil aggregates by the natural linear colloids, which is in many cases favourable for plant production, led to investigations with different synthetic, linear polyanions and with the technical product "krilium" (Söchtig, 1957; Flaig and Söchtig, 1957)

Polyacrylic or polymethacrylic acid, in some cases also cellulose derivatives such as carboxymethylcellulose, are used as model substances. "Krilium" consists of partially hydrolyzed polyacrynitrile or of a mixed polymer of vinylacetate and maleic acid. Field experiments have shown that "krilium" has in many cases a favourable effect on yield of crops but it is mostly too expensive for practical use. In the case of model experiments also the properties of polycations have been investigated. The positive charge of etheleneamine is higher than that of polyvinylpyrrolidone. The linear, heteropolar high molecular weight substances differ in their properties from the spheric ones (summary: Staudinger, 1941).

Strongly ionizable linear polymers such as polyacrylic acid are coiled in solution. With increasing sodium ion concentration the molecule is stretched out. With the addition of an excess of sodium hydroxide coiling occurs again. The effect on specific viscosity is greater the longer the chain length.
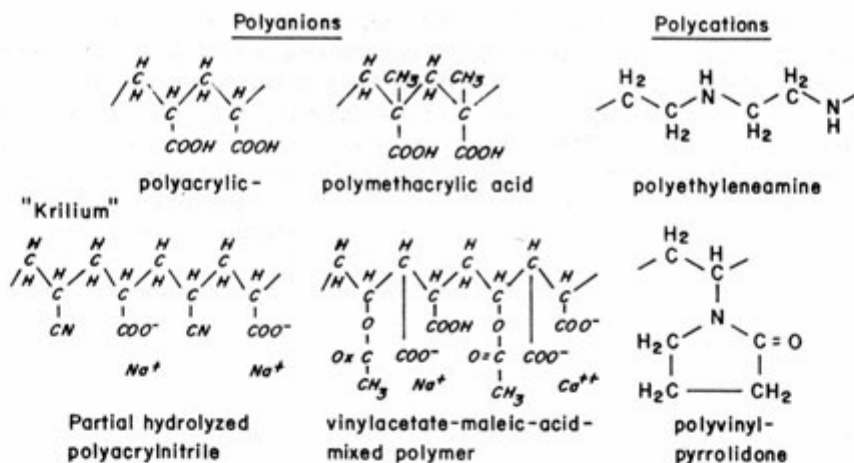
Fig. 26   Model substances

These properties of linear polyanions may play a role in the use
of such substances in practice. Soils under extreme climatic conditions
(salty soils, desert soils, etc.) usually need conditioning, because they
are not well textured. The aggregate stability in mixtures of linear
polyanions with inorganic soil colloids is caused partly by a different
mechanism to that in spherical organic colloids. No interactions between
sesquioxidehydrates and clay minerals are first necessary as in the case
of humic acids. In low concentrations filamentous, branched aggregates
of molecules, and in higher concentrations aggregates like a network,
are formed by drying. These processes are almost independent of the
pH value.
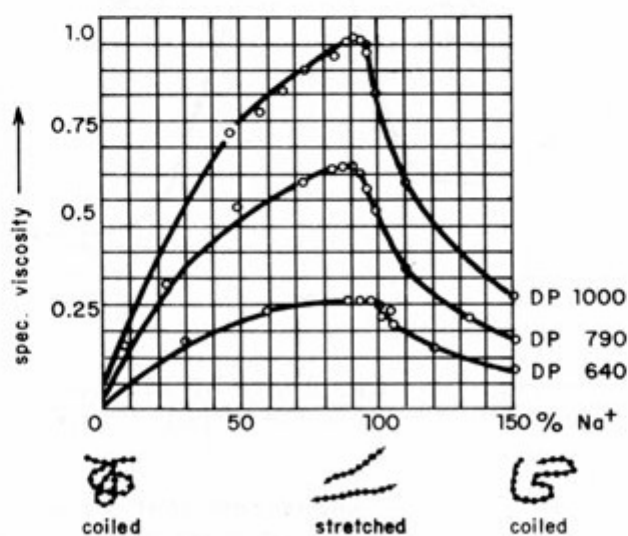
Fig. 27   Viscosity of a solution of polyacrylic acid depending
               on the concentration of sodium hydroxide

In model experiments with an electron microscope the differences in the effect of linear polymers in contrast to spherical polymers were demonstrated (Fig. 22). Also, in this case, the acidic groups interact with the kaolinite. This can be assumed because, after sorption of the linear polymer, the sum of cation exchange capacity does not correspond to the negative charge of clay mineral plus polymer. Other intermolecular forces are also effective. Furthermore, the single particles of the clay mineral are connected with filamentous aggregates of the molecules of the linear polymer. The effect on aggregate formation increases with the length of the chain of the polymer.

Long chained polyelectrolytes (anions and cations) also flocculate clay suspensions, as can be demonstrated by nephelometric measurements. In this case, cations play an important role, because with increasing concentration, coiling of the chain generally increases and this part of the effect on aggregate formation decreases. With an increasing addition of calcium chloride to a suspension of kaolinite and polyacrylate the flocculation increases. After the point of equivalence a complete dispersion occurs. This can be explained by coiling of the linear polymer molecules. According to these results, and others of further investigations, one can assume that the linear organic polyelectrolytes take a greater part in the processes of aggregation the more they are in stretched form. By adding of calcium chloride beyond the point of equivalence, flocculation again occurs. The different forms of the aggregates of the first flocculates and of the second lead us to assume that, in the case of the second flocculation, the clay mineral is co-precipitated contemporaneously with the clay mineral by the calcium ions (Flaig, Beutelspacher and Söchtig, 1958).
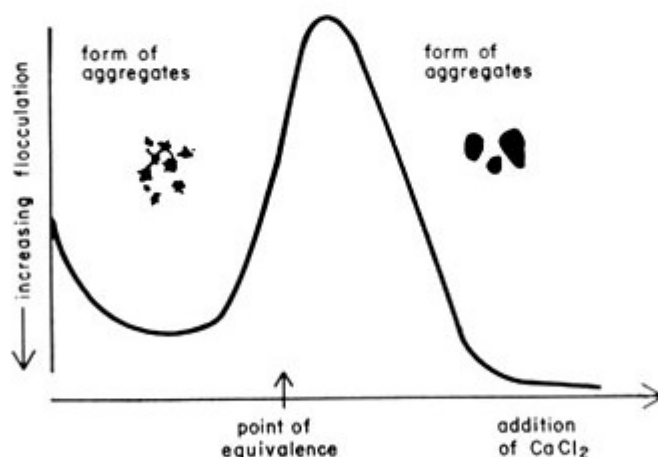
Fig. 28   Aggregation of kaolinite by addition of CaCl$_2$ in the presence of polyacrylate

These experiments demonstrate that the effect of "soil conditioners" consisting of negatively loaded polymers may also depend on the salt concentration in the soil solution. Therefore special investigations have to be made for each case, especially in salty soils. In Fig. 29 it is demonstrated that the flocculation of kaolinite is not only effected by the length of the chain but also by the charge of the linear polymers (Flaig, Beutelspacher and Söchtig, 1962). In the experiments described the suspensions contain the same amount of clay minerals and linear polymers;

they were added in different concentrations. When the chain length is equal, the positively charged polyethyleneamine is more effective over a larger range of concentrations in percent of added clay minerals than the less positively charged polyvinylpyrrolidone, which is more effective than the negatively charged polymethacrylic acid. These results might be interesting in connection with some natural linear polysaccharides with a different composition of monomers.

PK = polyethyleneamine
PVP = polyvinylpyrrolidone
PMA = polymethacrylic acid
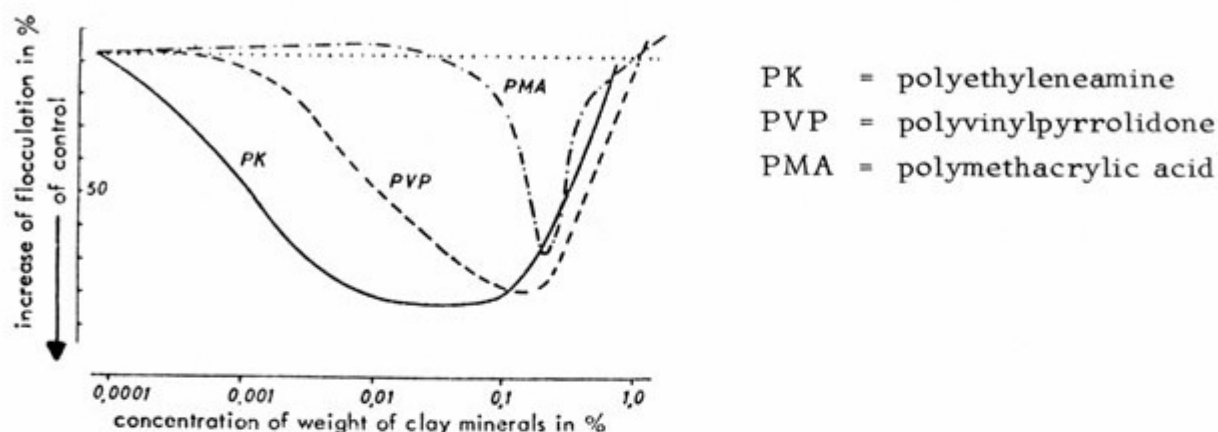
Fig. 29   Influence of differently charged linear polymers of equal chain length on the flocculation of kaolinite

It can be assumed that the contribution of naturally occurring linear polyanions to the soil structure is more effective if the mean residence time in soil is greater. This time depends on the resistance to microbial degradation.

Table 7   DECOMPOSITION OF ^{14}C-LABELLED POLYSACCHARIDES* FROM HANSENULA HOLSTII, LEUCONOSTOC DEXTRANICUS, AZOTO-BACTER INDICUS AND CHROMOBACTERIUM VIOLACEUM IN GREENFIELD SANDY LOAM
(Martin et al., 1974)

Organic amendment	Weeks Percentage decomposition**							
	1	2	3	4	6	8	12	16
H. Holstii polysaccharide 84% D-mannose, 16% D-mannose-6-phosphate	51	60	63	66	67	68	72	73
L. dextranicus polysaccharide dextran from glucose units	52	64	70	74	76	78	83	85
A. indicus polysaccharide 31% glucoronic acid, 16% aldoheptose 53% glucose	3	11	18	27	39	52	61	68
C. violaceum polysaccharide 16% glucoronic acid, 25% glucosamine 49% glucose	15	28	31	33	34	36	40	42
Oat straw	31	39	44	47	52	56	60	62
Corn stalks	31	40	44	46	48	49	55	57

* Decomposition in 500 g Soil at 60% of moisture capacity. ^{14}C-polysaccharides added at 0.25% concentrations.   ** Percent of added carbon evolved as CO_2.

Investigations of different ^{14}C-labelled polysaccharides isolated from cultures of bacteria and incubated in a soil under standard conditions demonstrate that, in general all those materials decomposed approximately to the same extent as oat straw or corn stalks after a longer time of incubation. But the rate of decomposition is slower in the case of the polysaccharides from <u>Azotobacter indicus</u> and <u>Chromobacterium violaceum</u> than in the case of the others. The polysaccharides of the two bacteria mentioned contain more acidic monomers in the chain than the others. One can assume that the polymers with stronger heteropolar monomers, such as glucuronic acid and/or glucosamine, are more adsorbed by the clay minerals of the loamy sand and therefore degraded more slowly.

Earth worm casts consist of very stable aggregates. After preparation for investigation with an electron microscope, filamentous particles were found, which may be the cause of the stability (Fig. 23).

In a manner similar to the effect of stretched linear polymers, the hyphae of fungi can act as crumb stabilizing material.

iii.   <u>Hydrophobic soil conditioners</u>

According to Lenvain and De Boodt (1975), the productivity of water repellent soils is a question of controlling the repartition and the quantity of hydrophobic substances in the soil. The addition of small quantities of hydrophobic bitumenous emulsion to soil decreases the evaporation and improves plant growth. The treatment of coarse volcanic soils from tropical regions with the emulsion mentioned has a beneficial effect on growth of grasses. Water losses are decreased, infiltration alters minimally and more water is available for plant respiration.

4.2.2. <u>Interactions Between Different Biopolymers in Soil</u>

Interactions between different organic colloids themselves are of importance for the conditions of life in and on the soil. These processes should be mentioned for two main reasons, because they:

i.   increase the persistence of linear colloids in soil, possibly by effecting aggregate stability;

ii.   stabilize the flow of nutrients for plant nutrition from soil organic matter, mainly in the case of nitrogen.

As little work has been done in this field to elucidate causal connections, further investigations are necessary.

i.   <u>Increase of persistence of high molecular weight compounds (e.g. chitin)</u>

It has already been stated that the fractions of humic acids also contain glucosamine-nitrogen (Chapter 3). Chitin, one of the linear polymers mentioned, synthesized mainly in the metabolism of mesofauna and fungi, is a polymer of acetylated glucosamine. For comparison, experiments have been made with chitosan, which can be extracted from the cell walls of <u>Mucor rouxii</u>.

Glucosamine is easily decomposable during incubation in soil. The addition of a preformed "model humic acid" synthesized by oxidation of phenols in the presence of a phenolase did not change the rate of decomposition. But, if the model humic acid was synthesized in the presence of glucosamine, the evolution of labelled carbon dioxide
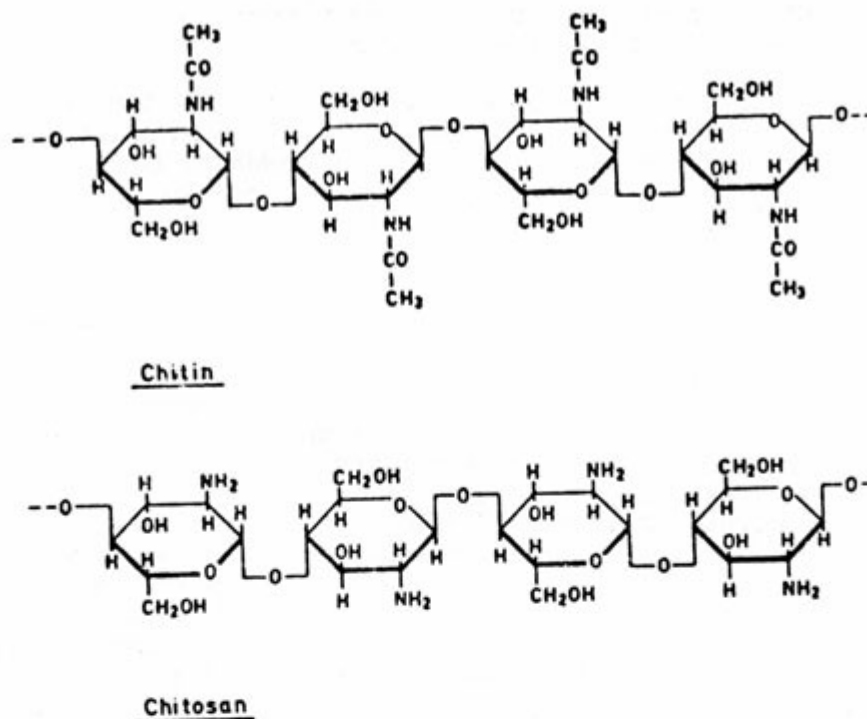
Chitin

Chitosan

Fig. 30   Formulae of chitin and chitosan

Table 8   DECOMPOSITION OF ^{14}C-GLUCOSAMINE (GA)* AND CHITOSAN
ADDED TO GREENFIELD SANDY LOAM
(Bondietti et al., 1972)

Amendment	Weeks					
	1	2	4	6	8	12
	cumulative % decomposition **					
Glucosamine	55	60	65	68	69	73
GA + phenolase model HA	51	57	62	64	67	70
GA incorporated into hydroxyphenol and hydroxybenzoic acid phenolase model HA	6	7	9	11	12	14
Chitosan	20	35	45	50	53	
Chitosan incorporated into phenolase model HA	16	23	27	29	31	

*   Decomposition in 500 g Soil at 60% moisture capacity. Samples added at
    0.25% concentrations.   ** Percent of added carbon evolved as CO_2.

decreased very much. The nucleophilic addition of the amino group of glucosamine to the ring of the intermediately formed semiquinones from the added phenols preserves the complexed glucosamine from rapid degradation by soil micro-organisms.

The same process occurs in the case of chitosan. A higher amount of labelled $^{14}CO_2$ evolution is observed in the case of incorporated chitosan than in incorporated glucosamine both in phenol humic acids. This is because degradation of the chain of chitosan occurs from the free end. That is the same phenomenon as in the case of amino acids and proteins mentioned above.

ii.   The role of soil organic matter as a slow release nitrogen source

Some remarks are necessary about the stabilization of the flow of nutrients for plant nutrition, especially nitrogen. The favourable effects of slow release nitrogen sources from fractions of soil organic matter for crop production have been mentioned in Chapter 3.

Verma, Martin and Haider (1975) investigated the decomposition of labelled proteins, peptides and amino acids in soil under standard conditions and found that after a 4 to 12 week incubation, 71-95% of the radioactive carbon was evolved as $^{14}CO_2$. The incorporation of these substances into model humic acids as described before reduced the rate of decomposition in some cases by between 80 and 90%. This means that during the formation of humic substances several reactions occur between the phenolic compounds and the protein-like materials which form part of the slow release nitrogen source, because by degradation of the carbon skeleton of the complexes nitrogen compounds, mainly ammonia, are also formed. The liberation of nitrogen from organic nitrogenous substances occurs mainly as ammonia. The lower the concentration of ammonium-ions in soil, the lower is the absolute concentration of nitrate formed by nitrification. The consequences are important for environmental protection, because the leaching of nitrates into deeper soil horizons and into groundwater is diminished.

Another aspect is that the probability exists that some of the lignin degradation products formed during humification of plant materials inhibit nitrification in soil (Flaig and Söchtig, 1967; Bundy and Bremner, 1974; see also Chapter 3). The properties of a technically synthesized, slow release organic nitrogen source should be those of a heteropolar high molecular weight polymer, possibly of linear shape and nitrogen in different organic linkages.

4.2.3   Influence of Soil Organic Matter on Soil Conditions by Retention of Certain Agrochemicals

In several cases it was observed that pesticides given to one crop damaged the growth of the next. The yield depressing effect was sometimes smaller when the content of organic matter was larger in the soil.

Attempting to throw light on the causal connections, it was found, for instance, that the adsorption of "Disulfoton" {(diethyl-S-2-ethyl-thio)-ethylphos-phorthiolthionate} is correlated more with the organic carbon content of the soil than with its cation exchange capacity or its clay content (Fig. 31). This correlation exists for other types of pesticides. The degree of sorption is a function of chemical structure (summarized in: Weed and Weber, 1974). The sorption and possible consequent stabilization or slow release of these compounds are still poorly known and would be worthwhile subjects for future research.

Properties of soils.

No.	pH	CEC meq/100g	Clay %	Organic carbon %
1	8.1	6.3	8	0.7
2	8.1	10.4	18	0.9
3	6.8	10.2	6	1.1
4	6.8	10.6	6	1.3
5	7.5	13.0	26	1.4
6	8.0	21.9	36	1.7
7	8.1	10.6	10	1.7
8	7.2	14.0	21	1.8
9	6.5	10.7	7	1.8
10	7.8	19.8	18	2.7
11	6.3	18.2	2	2.8
12	7.5	44.8	11	7.6
13	7.7	48.2	16	8.8
14	7.6	74.0	36	11.0
15	7.2	66.4	25	12.0
16	5.1	83.4	62	15.0
17	6.9	118.8	peat soil	31.0
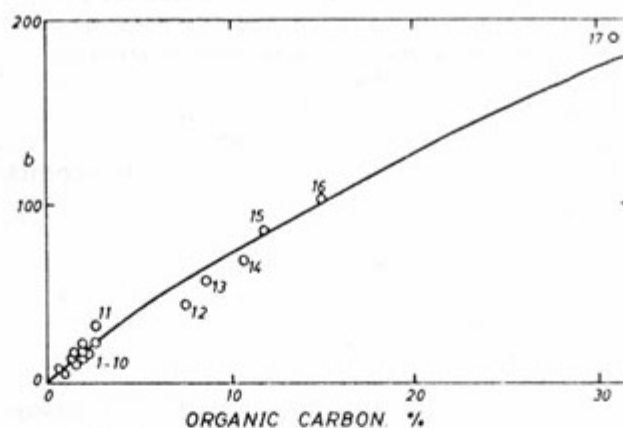
Fig. 31   Relationship between organic carbon content of soil and adsorption of pesticides (Graham-Bruce, 1967)

In connection with the dynamics of soil organic matter it should be mentioned that different authors found that decomposing plant material in the field (Williams, 1968) or in model experiments (Walker and Crawford, 1968) adsorb higher amounts of pesticides per gramme of soil carbon than does more highly humified organic material in soil. Some authors (Hance, 1969; Süss and Wagner, 1969) assume that the humic acids as such are not the constituents of soil organic matter that are most effective in the sorption of pesticides. This means that possibly some of the pesticides might participate in the reactions during formation of humic substances. However, van der Waal's forces could also be responsible. Thus, for instance, Sullivan and Felbeck (1968) tentatively propose a mechanism for the adosrption of atrazine by alcoholic extracts of humic acids. Changes observed in the infra-red spectra, following formation of the atrazine-humic acid complex, suggest that the carboxylic and phenolic hydroxyl groups of the humic acids interact with the nitrogen atoms of the alkyl-amino substituted s-triazines.

4.3 INFLUENCE OF SOIL ORGANIC MATTER ON THE AVAILABILITY OF PLANT NUTRIENTS

Soil organic matter, as well as added organic material, act not only as a source of nutrients (see section 4.1) but also influence the availability of nutrients in different ways. During the process of chemical weathering (see Chapter 2), organic acids formed in the transformation cycle of soil organic matter and also those excreted from living organisms can contribute to the solubilization of nutrients from the mineral components of soil or parent material (e.g. Boyle et al., 1974). The soil organic matter is the most effective cation exchanger (see Chapter 2) and thus stores the nutrients against leaching. Scheffer and Ulrich (1960, p. 212) indicated that, based on the Donnan equilibrium in soil organic matter, relatively more divalent cations can be adsorbed; consequently, more monovalent cations can either be taken up by plants or leached.

The effect of organic fertilizers and soil organic matter on availability of phosphate is mainly due to the complex formation of bi or trivalent cations which inhibit the formation of non-available forms of inorganic phosphates. Struthers and Sieling (1950) found that in nine tested organic acids, produced in soil by

micro-organisms, citric acid was the most effective among oxalic, malonic, malic and lactic acid to prevent the precipitation of phosphate by iron and aluminium. The effectiveness increases with the number of acid groups and decreases with chain length. The same action was found with humus substances (Swenson et al., 1949; Graham, 1955; Okuda and Hori, 1957; Williams, 1960; Domaar, 1963), phenolics (Appelt et al., 1975) and several sugars (Bradley and Sieling, 1953). The effect is observed chiefly after the addition of easily decomposable organic material (Dalton et al., 1952) and under calcareous soil conditions (Khanna and Roy, 1956).

The effect of organic material seems to be dependent not only upon the relative amount of the reactive components but also upon the stability of the organic compounds involved. In experiments with red lateritic soils (Söchtig, unpublished) it was observed that the extractability of phosphates was higher, if the phosphate fertilizer was added to the soil together with an organic nitrogen fertilizer (N-lignin made by oxidative ammonization of sulphite liquor of pulp and paper industries), than without it. But the extractability decreases with time and the same low level of extractable phosphate is reached after 4 weeks. Another addition of the organic nitrogen fertilizer again increases the extractability for a short time. This short time, nevertheless, affects the uptake of phosphate by plants. On the other hand, the content of phosphate in plants grown on soils poor in phosphate is higher when N-lignin is added simultaneously due to its action as a nitrification inhibitor by a change of the cation anion-equilibrium (Söchtig, 1970) and/or by better root development as observed after nitrogen fertilization by Grunes and Krantz (1958).

The ability of organic compounds to form complexes and/or chelates with cations influences not only the availability of phosphate but also that of the metal cations needed by plants. Dolar et al. (1971) stated that there was a positive correlation between the content of organic matter in soil and the extractability of trace elements. The positive effect on iron chlorosis obtained by adding iron chelates is well known (Steward and Leonhard, 1957; Bould, 1955; Wallace et al., 1955). The addition of water soluble, chelate forming organic compounds to a soil can improve the supply of trace elements to plants (Perkins and Purvis, 1954; Butler and Bray, 1956; Holmes and Brown, 1955). Christenson et al. (1951) and Lindsay and Norrell (1969) show that the process of chelate formation depends, among other things, on the pH of the soil, the concentration of other cations present in the soil solution and the type and amount of organic substances in soil.

The formation of unavailable complexes can reduce the uptake of copper by plants (Gilbert, 1952). Schlichting (1955) discussed the question of the formation of soluble and insoluble complexes in different extraction conditions. Elgala and Schlichting (1976) reported that the addition of humic acids to a soil increases the extractability of iron, manganese, zinc and copper; this extractability decreases with the length of incubation, mainly for copper and zinc. Additionally, solubilization of iron and manganese can be enhanced by reduction of non-available higher oxide forms to available in the presence of organic material. This effect is stronger under natural reducing conditions, as in water-logged soils (Piper, 1931; Mann and Quastel, 1946; Bloomfield, 1951; Motomura, 1962). The same effect can be observed if large amounts of plant residues are incorporated in well-drained soil (Betremieux, 1951; Cotter and Mishra, 1968; Elliot and Blaylock, 1975). Behrenberg-Goszler (1943) observed that in a field with a manganese deficiency the plants growing in the tractor tracks are normally coloured and healthy.

4.4 INTERRELATIONSHIPS BETWEEN ORGANIC AND MINERAL FERTILIZERS IN SOIL PRODUCTIVITY

For many investigations [1] it is known that fractions of humic substances can have a favourable effect on growth and yield in nutrient solutions, sand cultures as substrate for cultures and also in soil. However, other results are published which do not confirm the favourable effect of humus or its fractions (summarized in Sax, 1963). An endeavour was made to elucidate and summarize these contradictions in Söchtig (1964).

The extent of the influence of metabolically active substances also depends on environmental conditions such as temperature, light and humidity, as well as on nutrient supply. Some examples may explain this, for instance, Chaminade (1966, 1968) found that overdoses of inorganic nitrogenous salts remain effective for yield production in the presence of humus, while without humus there was a decrease in yield. The investigations were made in pots with sand cultures and rye grass. Charreau (1975) also observed a favourable effect on crop yield by adding organic material to ferralitic soils whereby there was a better utilization of nitrogen.
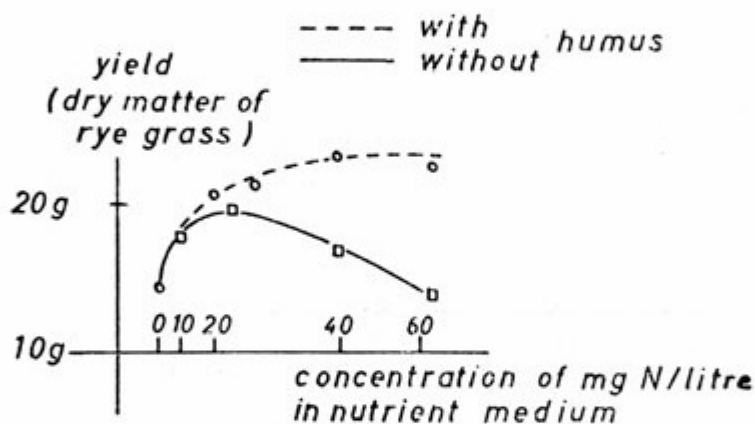
Fig. 32   Influence of humic substances on yield with overdoses of inorganic nitrogenous salts (according to Chaminade, 1966)

Several laboratory experiments were made to explain the possible mechanism of the effects observed. Guminski and Guminska (1953) investigated the influence of fractions from humus on the production of plant mass or tomatoes at low oxygen tension in water cultures (Fig. 33). The yield from an unaerated nutrient solution was higher when humic substances were added than without them. But the yield was the same in an aerated culture with and without the addition of humic substances.

In pot experiments Söchtig (1964) investigated the influence of a model substance from ozidized lignin degradation products; the substance was thymohydroquinone (THQ) (Fig. 33). The soil was constantly saturated and the water flow was about 100 ml. The leaching of nutrients was not influenced by the addition of THQ. In spite of these unfavourable conditions, such as leaching of

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[1]   Blanchet, Chaminade, Christena, Guminski, Part and co-workers, Nielewski, Rypacek, Sladky, Saalbach, Söchtig, Tichy and others summarized in Flaig, 1968

Table 9   EXPERIMENT ON THE SPECIFIC ROLE OF ORGANIC MATTER BAMBEY, SENEGAL, 1972 [1]

A - Yields of early pearl millet (kg/ha)

	Addition of composted straw	Mineral nitrogenous fertilizer (N kg/ha)					
		0	30	60	90	120	150
Grain	11 t/ha (D.M.)	1 959	1 971	2 179	2 241	2 192	2 061
	0	1 608	2 017	1 956	2 039	1 959	1 922
Straw	11 t/ha (D.M.)	6 325	6 600	7 250	7 025	7 210	7 480
	0	4 825	6 375	6 375	6 040	6 925	6 170

B - Distribution in % of fertilizer nitrogen stored in the various parts of the soil-plant system (calculations from ^{15}N)

Fertilizer	Addition of composted straw	Straw	Grain	Straw + Grain	Soil (0-90 cm)	Soil + Straw + Grain	Losses
90 N	11 t/ha (D.M.)	18.8	17.6	36.4	37.7	74.1	25.9
	0	18.0	21.2	39.2	43.3	82.5	17.5
150 N	11 t/ha (D.M.)	16.5	11.1	27.6	29.5	57.1	42.9
	0	14.9	12.7	27.6	25.0	52.6	47.4

C - Percentage of total nitrogen in grain and straw coming from fertilizer (calculations by usual methods)

Fertilizer	Addition of composted straw	Straw	Grain	Straw + Grain
90 N	11 t/ha (D.M.)	22.9	21.7	22.2
	0	16.4	26.5	20.6
150 N	11 t/ha (D.M.)	22.3	28.3	24.3
	0	33.4	37.0	35.3

[1]   Source: Dommergues (1973). After: Ganry (1973); Guiraud (1972)

nutrients, water saturation of soil and low oxygen tension, the hydroquinones increased the yield remarkably (up to 13 g), but not up to the amount of the control (29.2 g) without leaching of nutrients and water saturation of the soil.
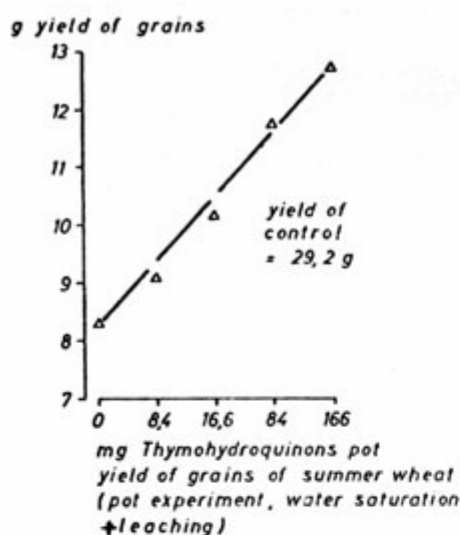
Fig. 33 Investigation of oxygen deficiency in nutrient cultures (Guminski)
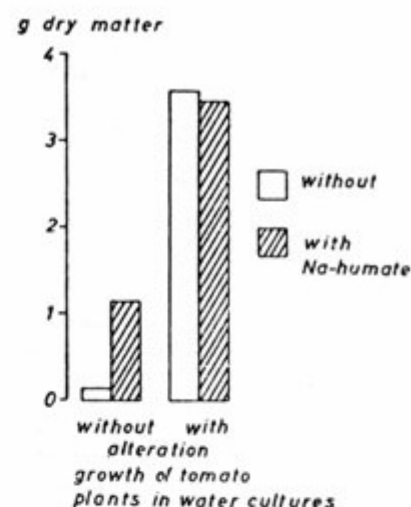
Fig. 34 Investigation of the leaching of water in the presence of thymohydroquinone (Söchtig)

Boguslawski and Saalbach (1960) observed that the effect of thymohydroquinone depended on the different climatic conditions occurring during the four years of a field experiment and on an intensive interaction with the nitrogen supply of the plants. The effect of THQ on the growth of seedlings depends on humidity. The dry weight of the seedlings was increased by THQ only at lower humidity, while there was no effect at 100% humidity. The content of reducing sugars in the treated plants was higher than in the untreated; therefore the osmotic value was higher in the former plants. They did not wilt at low humidity as did the control. The treated plants had a greater resistance to drought, and also to frost (Söchtig, 1964). These and other experiments demonstrate that the effect of a metabolically active substance on plants depends on the environmental conditions (see also Söchtig, 1967).

Table 10   INFLUENCE OF HUMIDITY ON THE EFFECT OF THQ ON THE INITIAL GROWTH OF SUMMER RYE
(Saalbach, 1957)

	Sprouts			Roots	
mg/l THQ	dry weight rel.	content of reducing sugars	water	dry weight rel.	content of reducing sugars
		mg %	%		mg %
100% humidity					
0	100 (0.89 g)	200	93.0	100 (0.32 g)	25
1.7	97	180	93.0	109	40
16.6	100	165	93.3	159	55
55-60% humidity					
0	100 (0.75 g)	200	91.5	100 (0.38 g)	25
1.7	125	305	90.6	132	40
16.6	116	360	91.0	155	25

Underlined values statistically significant.
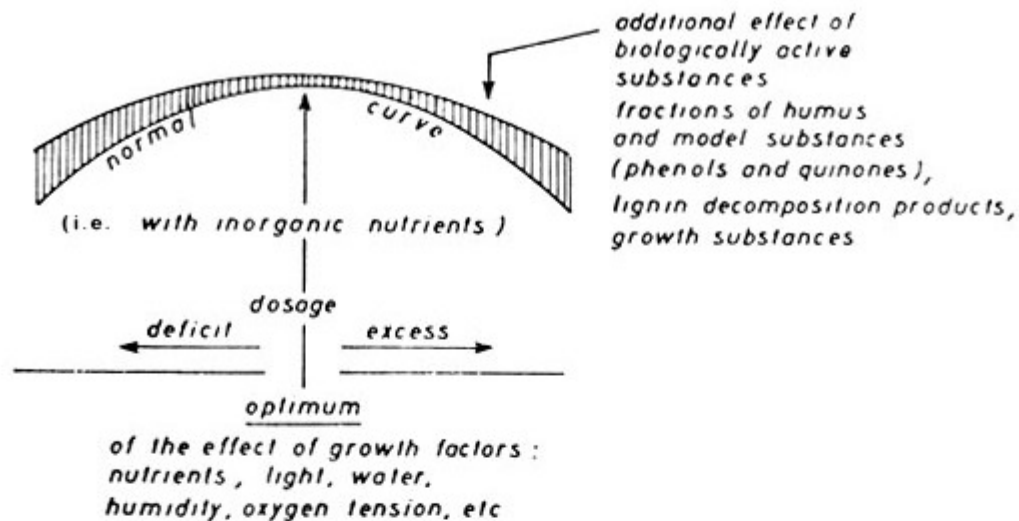
Fig. 35   Influence of physiologically active substances on
               yield and its dependence on environmental factors

        The favourable effect of humus on plant growth and yield can be explained
in the following way: when growth factors, such as temperature, humidity, light,
oxygen tension of the culture medium and water saturation of the soil, as well as
the supply of nutrients are optimum, the yield of the plant mass is highest. In
other words, the effect of physiologically active substances improves the yield
formation, if one or several growth factors are deficient or excessive. This
explanation of the effect of substances from humus, lignin degradation products
or other physiologically active substances, helps to explain some of the contra-
dictory results in literature. Economically, the results can mean a partial
diminution of the risk of lower yields caused by components of soil organic matter;
a risk depending on climate factors, heavy rainfall, dry seasons and other
abnormal conditions.

4.5   BIOTIC NITROGEN FIXATION

        Fixation of nitrogen by lower organisms in soils for the nutrition of plants
occurs mainly through:

        i.   free living organisms such as algae and bacteria
                (asymbiotic fixation)

        ii.   lower organisms (Rhizobium) living in symbiosis with
                special species of plants such as leguminosae, alder,
                tamariscs, etc.

        iii.   a system of semi-symbiotic fixation by micro-organisms
                living mostly in the rhizosphere of tropical gramineae.

        The effect of biotic nitrogen fixation in soil depends on environmental
conditions, e.g. composition of the soil, soil structure and climatic factors.

        To compare the effect of biotic nitrogen fixation with other nitrogen
sources, some data for temperate zones are given in Table 11.

Table 11   NATURAL NITROGEN SOURCES

	kg/ha/year
Mineralization of soil organic matter from which about a third is used for plant nutrition (reserve of organic bound nitrogen in mineral soils 900-9 000 kg/ha)	30-270
N-fixation by free living bacteria	10
N-fixation by symbiosis (leguminous crop)	100-200
From atmosphere by precipitation	10
Addition of organic manures	40

4.5.1 Asymbiotic Fixation

The free-living nitrogen fixing organisms have their optimal growth under different soil conditions. The C/N-ratio of soil organic matter as the source of energy must be high to transform the molecular nitrogen to proteinaceous nitrogen. Among the bacteria: Azotobacter has its best living conditions in well-aerated soils with neutral reaction, Bacillus amylobacter and Chlostridium occur in many soils with a wide pH-range, Beijerinckia is adapted to acid soils because of the low calcium requirement and is distributed in lateritic soils in the tropics. Some fungi participate as free-living organisms in nitrogen fixation.

Other nitrogen fixing organisms have a special importance for food production from graminaceous plants, e.g. rice in developing countries. These are blue-green algae such as Nostoc, Calothrix, etc. In the humid tropics some nitrogen fixing bacteria live on the leaves and provide a direct supply of nitrogen. The ability of lichens to fix nitrogen plays a role when plants are first grown on raw soils.

According to the data in Table 11 the amount of nitrogen fixed by asymbiosis is not high and therefore not of such economic importance as symbiotic and 'semi-symbiotic' nitrogen fixation.

4.5.2 Symbiotic Fixation

Each species of leguminosae needs its own species of Rhizobium which is an organism that acts through nodules on the roots. The nitrogen fixing capacity of the bacteria depends on the plant's growth conditions. About 50% of the relatively large amount of nitrogen fixed remains in the roots and stubble on the fields. During humification of these materials the next crop (e.g. cereals) can make use of the nitrogen produced for its own nutrition.

About 13 000 leguminosae are known, but only a very few are used in agricultural production. The selection of new varieties for food production is an important task for plant breeders. The species of Rhizobium must be adapted to the particular leguminous plant. The inoculation of seeds increases nitrogen fixation if the specific bacteria are not yet present in the soil to be cultivated. The selection of more or less effective strains by microbiologists can be made in routine work by measuring the reduction of acetylene to ethylene by the nitrogen fixing enzyme system, nitrogenase (Dillworth, 1966; Schöllhorn and Burris, 1966).

4.5.3 'Semi-symbiotic' Fixation

The hope that one day in the future the symbiotic fixation of nitrogen might be extended to other non-leguminous crop plants and the possibility of measuring nitrogenase activity gave new impetus to research on biotic nitrogen fixation and its use for plant production. It was found that bacteria living in the rhizosphere of tropical grasses fix a remarkable amount of nitrogen. According to first calculations, the fixation reaches 60 kg N/ha in rice fields (Yoshida et al., 1973). Azotobacter, Beijerinckia, Pseudomonas and Anthrobacter have been identified (Balandreau et al., 1975) as fixing bacteria.

Furthermore it has been demonstrated that several nitrogen fixing bacteria occur on the roots of sugarcane, Bahia-grass and other grasses, which are used to feed cattle (Döbereiner, 1968; Döbereiner et al., 1974 a, b). The same authors found that temperatures below 27°C during the day and below 18°C at night inhibit nitrogen fixation. By this 'semi-symbiotic' nitrogen fixing system up to 1 kg N/ha/day should be fixed by tropical grasses for feedstuffs. In one case it was proved, by using nitrogen-15, that about 75% of the fixed nitrogen is utilized by the plant.

Two theories exist about nitrogen fixation which have not yet been described in detail or proved. Schanderl (1947) discusses special organelles in all plants for molecular nitrogen utilization, while Dhar (1968, 1972) explains nitrogen fixation by processes deriving energy from the sun and the organic part of the soil. It is to be hoped that practical application of this new knowledge will increase world food production through the supplying by the plant itself of the required nitrogen. Concerning soil organic matter, possible interactions between its constituents and nitrogen fixation have not yet been studied. But one should keep in mind the results of soil biologists, because it is known that high doses of organic materials increase the yield of rice fields. Some interesting genetic work is also in progress.

5.1   CHARACTERISTICS AND PROCESSING OF DIFFERENT ORGANIC MATERIALS FROM NATURAL SOURCES

5.1.1   Animal Manure

Since the beginning of livestock husbandry, animal excrement has played a role of changing importance, being considered either as an inconvenient, difficult to dispose of by-product or as valuable manure for soil improvement and crop production.   Historically, the agricultural significance of animal manure was recognized more than 2 000 years ago (Xenophon, 400 BC), and there is no evidence to deny its use by pre-historic farmers.

There are also non-agricultural uses for excrement, such as bricks or 'mortar' for houses and buildings, in "wurtes" (small mounds for protection against floods), as medical drugs for external and internal use.   In many dry or treeless regions, it was and still is an important fuel: buffalo chips were collected to heat sod houses on the Great Plains;   cakes were formed and dried for burning on the islets in the Baltic Sea as well as throughout the Middle East and India.   For 200 years man has known about the burnable gas, methane, which develops from manure by micro-organism activity under anaerobic conditions (Fig. 36).
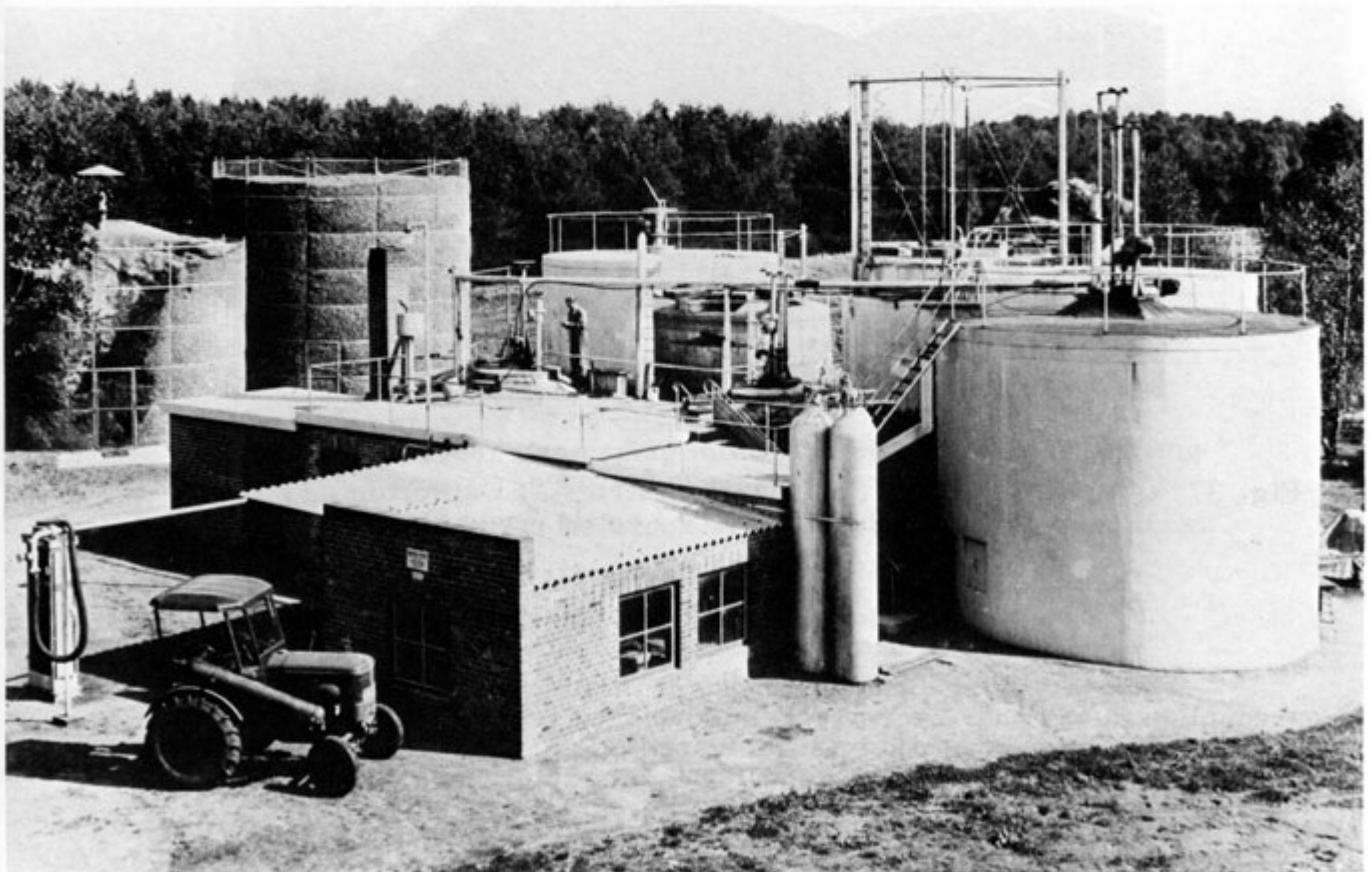
Fig. 36   Manure gas plant in Germany

In many areas livestock farmers regard animal excrement as useless dirt. They handle it as waste, like the ancient King Augeas at Elis whose stable was cleaned out in one day when Hercules diverted a river through it - a significant performance but not recommendable for imitation because of the ensuing heavy river pollution.

The manure map of the world by Mather (1956) demonstrates that farm manure has been a primary concern of European farmers. It is of agricultural significance in those favoured localities where animal husbandry is closely associated with crop production. Waste or accumulation of manure occurs in those areas where this relation does not exist, i.e. where livestock management in feedlots prevails. Figure 37 shows "Mount Fertilizer" in Artesia, California, which is a hill of cattle manure.

Fig. 37   "Mount Fertilizer" in Artesia, California
(about 30 000 m^3 cattle manure)

The decreasing quantity of manure in the nutrient supply to crop production in Germany over nearly one hundred years is compared to the increasing portion of commercial fertilizers (Fig. 38). The observed decrease in manure relates only to the percentage of the total nutrient supply.

Where there is an interrelation between animal husbandry and crop production, success can be achieved by increased manure production and application. The dilemma described in an old Flemish proverb must be overcome: "Point de fourrage, point des bétail - point des bétail, point de fumier - point de
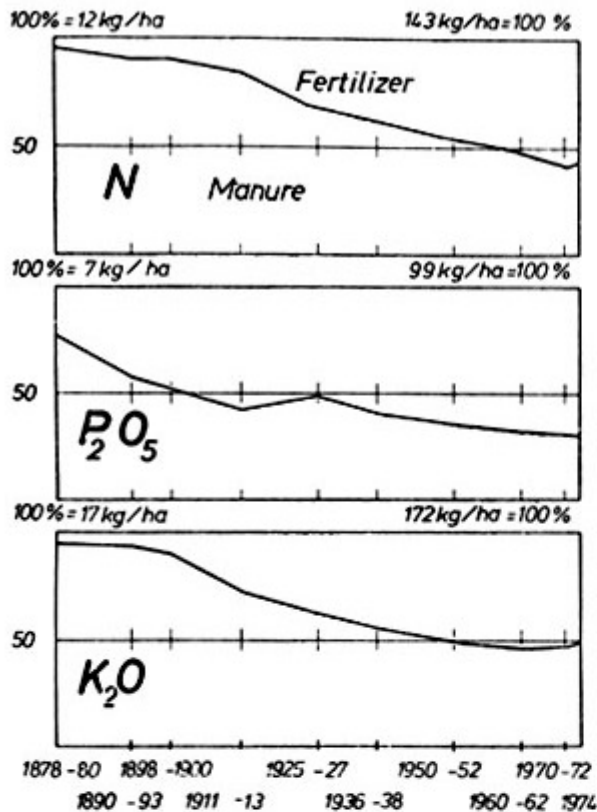
Fig. 38

Nitrogen, phosphate and potash nutrients applied in crop production from 1878-1974 in Germany. Change of portions applied with commercial fertilizers and with livestock manures

$$P_2O_5 \times 0.44 = P$$

$$K_2O \times 0.83 = K$$

fumier, point de fourrage". As shown in the past, the key to success lies in intensifying and improving forage growing through the following sequence:

Improve forage production by

- increasing the area
- improving grassland management, hay making and forage conservation
- growing leguminous plants as the main crop in the rotation
- growing catch crop fodder
- increasing grazing intensity, but decreasing grazing periods in favour of stabling and indoor-feeding.

Increase the livestock with improved feeding practices.

Improve manure utilization by

- total collection of liquid and solid excrement
- nutrient conserving treatment and storage
- application at the right time using procedures best fitted to the crop and the site.

Uniform distribution of liquid manure on cropland is shown in Figure 39, while Figure 40 shows steaming, solid manure with litter being scattered with a manure spreader. These illustrations distinguish between the rotting process of solid manure at high temperature by self-heating and the "cold fermentation" of liquid manure in a pit or silo where air access is prevented and no losses occur.

Fig. 39   Uniform distribution of liquid manure on cropland

Fig. 40   Steaming solid manure distribution with a manure spreader

Livestock manures contain organic matter and nutrients, both of which are valuable for improving and conditioning the soil and for the nutrient supply of the crop. The significance of the nutritive substances is greater where other sources are not available and in periods of shortage of commercial fertilizer supply.

i.   Quantity of excrement in relation to animal live weight

Estimates of the amount of excrement, faeces as well as urine, and their analytical data will always show a great variation. There are many effective influences depending on the animal and on environmental factors.

The data in Tables 12 and 13 are based on comprehensive feeding experiments with weight control and analyses of many samples. They show, for example, the relation between animal weight and the amount of faeces and urine excreted daily and also the influence of pregnancy (Sauerlandt, 1970). With regard to the content of crop nutrients, fresh manure from laying hens ranks first, followed by pig and cow manure; the latter has a high potassium content. The graphs in Figures 41 and 42 were developed from the data in Tables 12 and 13. They represent the amounts of manure and nutrients from cows in a period of 1 000 animal-days and from pigs in 10 000 animal-days. The increase of the total mass by combined collection of faeces and urine is shown and also the changing

Table 12   FAECES AND URINE EXCRETED DAILY BY DAIRY COW AND FATTENING PIG

	Faeces kg	Urine kg	Faeces + Urine kg	Faeces	Urine	Faeces + Urine
				% of live weight		
Dairy cow, 630 kg						
During lactation	34.4	21.2	55.6	5.5	3.3	8.8
During pregnancy	23.4	20.4	43.8	3.6	3.2	6.8
Average	29.5	20.8	50.3	4.6	3.3	7.9
Fattening pig, cereals						
Live weight 40 kg	1.02	2.60	3.62	2.4	6.2	8.6
60 kg	1.51	2.57	4.08	2.5	4.3	6.8
90 kg	1.90	2.55	4.45	2.1	2.8	4.9
130 kg	2.15	2.74	4.89	1.7	2.1	3.8
Average 87 kg	1.73	2.62	4.35	2.0	3.0	5.0

Table 13   CONTENTS OF NUTRITIVE ELEMENTS IN TOTAL EXCRETA CALCULATED ON A FAECES/URINE RATIO OF 3:3 FOR DAIRY COW AND 2:3 FOR FATTENING PIG, % FRESH

	N	P	K	Ca	Mg
Dairy cow	0.46	0.07	0.48	0.29	0.06
Fattening pig	0.91	0.29	0.28	0.34	0.06
Laying hen in coop	1.53	0.47	0.49	0.87	0.17

Cows: Excrement (t) and Nutrients (kg) per 1000 Animal-Days
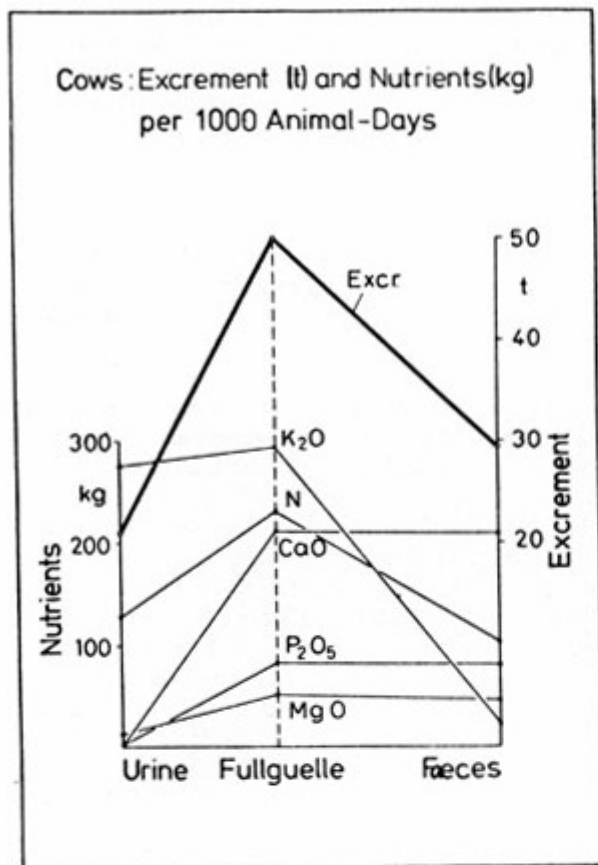
Fig. 41

Faeces and urine (t) from dairy cows, mass and plant nutrients per 1 000 animal-days

Fig. 42

Faeces and urine (t) from fattening pigs, mass and plant nutrients per 10 000 animal-days

Pigs: Excrement (t) and Nutrients (kg) per 10000 Animal-Days
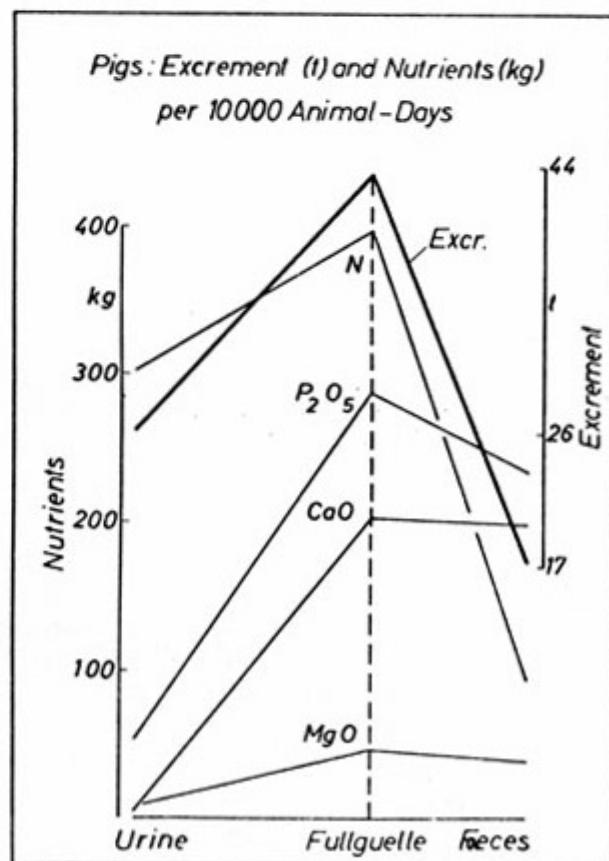
ratio of nutrients. Because of the low contents of Ca, P and Mg in urine, these quantities are not remarkably influenced by increasing portions of urine. Potassium (shown only for cows) and nitrogen show a steep increase with the proportion of urine. The ratio of nutrients shifts continuously, thus influencing the fertilizing effect on crop growth. This demonstrates the difficulty of matching the nutrient demand of crop and soil with liquid-manure application without some kind of standardization by well-adjusted mechanical equipment for the procedural steps of collection of faeces and urine, storage and treatment, mixing, loading and uniform spreading.

ii.   <u>Factors affecting manure and nitrogen yielding portion</u>

The effect of manure on soil conditioning and crop yield depends on several factors; the influence of three of these factors is shown in Table 14 and they are:

a.   the means of manure distribution on the land: a pitch fork gives only a coarse distribution; a manure spreader gives a fine, closed cover; liquid manure penetrates at once into the upper layer of the soil, thus decreasing loss of volatile matter;

b.   the ratio of carbon to nitrogen, which is influenced by various treatments that decrease the loss of nitrogen or accelerate the decomposition process of organic matter; in general, the narrower the C/N ratio, the higher the manure effect on crop growth;

c.   the available nitrogen portion of total nitrogen in the manure depends again on various treatments; the greater the urine portion together with an appropriate quantity of water added, the higher the contents of NH_4-N.

Depending on different arrangements of these three factors, various effects on crop yield can be observed, ranging from depressing to very high. According to this scale, only liquid manure has a high or very high yield effect.

<u>Table 14</u>   EFFECT OF MANURE ON CROP YIELD INFLUENCED BY
TYPE OF SPREADING, RATIO OF CARBON TO
NITROGEN AND PORTION OF AVAILABLE
NITROGEN

Spreading	C/N	Available nitrogen	Effect on yield
1. Coarse	20:1	Medium	Low
2. Fine	20:1	Portion	>1
3. Liquid	20:1	of N total	>2
4. Coarse	15:1		>1
5. Liquid	15:1		High
6. Coarse	20:1	Great	= 4
7. Liquid	20:1	Portion	4-5
8. Fine	15:1		= 7
9. Liquid	15:1		Very High
10. Coarse	25:1	Small	Depressing
11. Liquid	25:1	Portion	>10

Results of field and pot experiments with various kinds of manures have been summarized in Figure 43 to demonstrate the differences in yield effect. The basis of comparison was the amount of nitrogen applied with the specific manure and the effect on yield of known amounts of mineral nitrogen fertilizer, thus showing the portion of total nitrogen in the manure which has an effect on crop yield. This figure shows that, generally, the nitrogen in urine has about the same effect on crop yield as mineral nitrogen; 100 nitrogen units in solid barnyard manure are equal to 0-30 units in mineral fertilizer. The broad range between barnyard manure and urine is created by various kinds of gülle. Gülle with litter is in the lower range and gülle without litter is in the upper range. A so-called "Full gülle", which contains the solid and liquid excreta from animals, is classified at about 50. Collection and storage of barnyard manure and gülle differ not only in the fact that gülle contains all urine but, in addition, gülle stored in a pit with restrained air access retains almost all its plant nutrients.

The Yield Effective Nitrogen Portion in Solid and Liquid Manures

GÜLLE   Urine
with litter   without litter
Manure
0   30   90   100
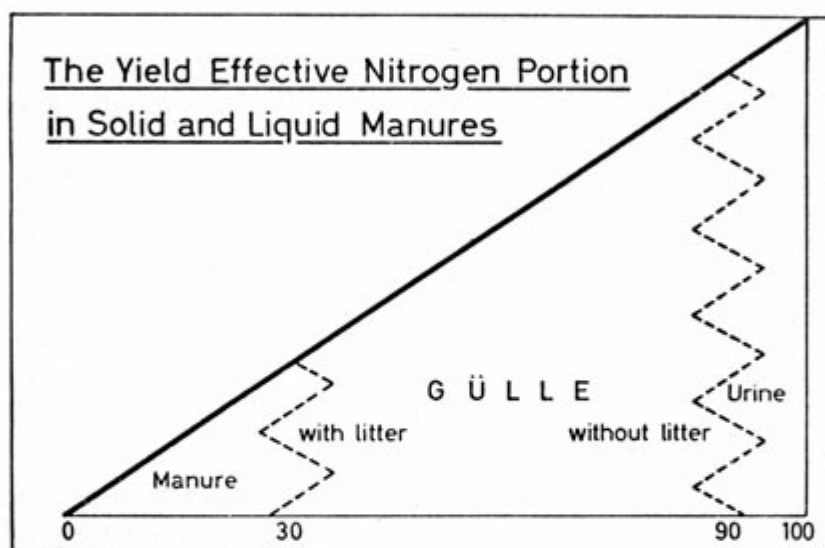
Fig. 43   Solid and liquid manure classification according to portion of nitrogen effective on crop yields

Figure 44 shows the two year results of two field experiments with different manures at the same location. Equal amounts of fresh excreta and litter were stored for eight weeks, on the one hand in a heap and on the other hand in air-tight concrete pits. One closed pit was heated to 30°C to produce manure gas by the decomposition of carbonaceous material; the other one was not heated and its temperature was about 15°C. These manures were then applied to potatoes. Equal amounts of mineral phosphate and potassium fertilizers were employed, while three stages of nitrogen application were differentiated. Average yields in the first year were significantly higher than in the second year because of different weather conditions. However, in both years the same trend was observed: variants Nos. 1 and 2 (no manure and barnyard manure) showed the well-known yield increase by nitrogen application. The reciprocal effect of both liquid manures - gülle I and gülle II - and nitrogen fertilizer showed a noteworthy result. High yields were obtained by the liquid manures without nitrogen fertilizer. Variant 3 with the narrower C/N ratio, as a consequence of the heat treatment, proved superior to variant 4. Nitrogen fertilizer did not remarkably increase the yield of those manures.

Potatoes, 1957, 1958

	Fertilizer N kg/ha					
	0	30	60	0	40	80
1 No Manure	30,9	35,5	37,1	19,3	24,0	26,7
2 Barnyard Manure	33,6	37,3	37,2	23,3	26,9	29,2
3 Gülle I	37,6	36,7	35,5	27,5	27,1	25,7
4 Gülle II	—	—	—	25,7	27,9	26,9
LSD 5%	25	18	27	23	2.7	3.7

Fig. 44

Reciprocal effect of nitrogen fertilizer and manures on yield of potatoes, 1957 and 1958
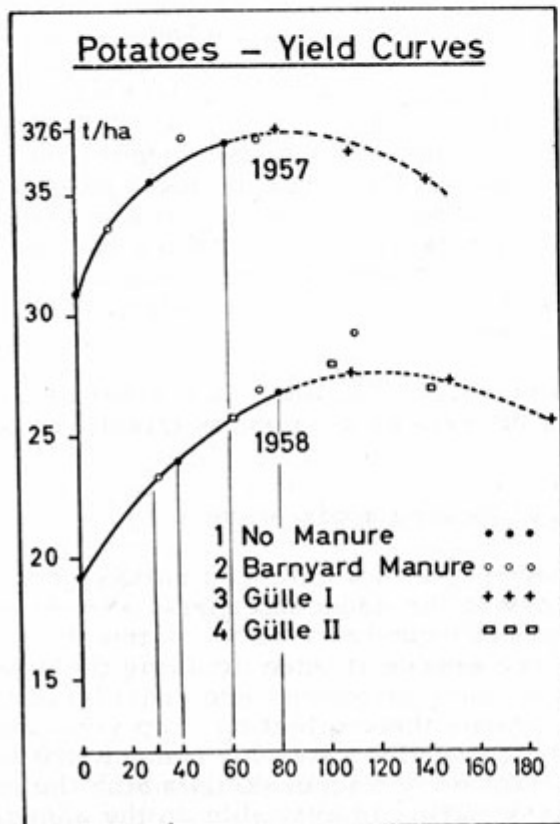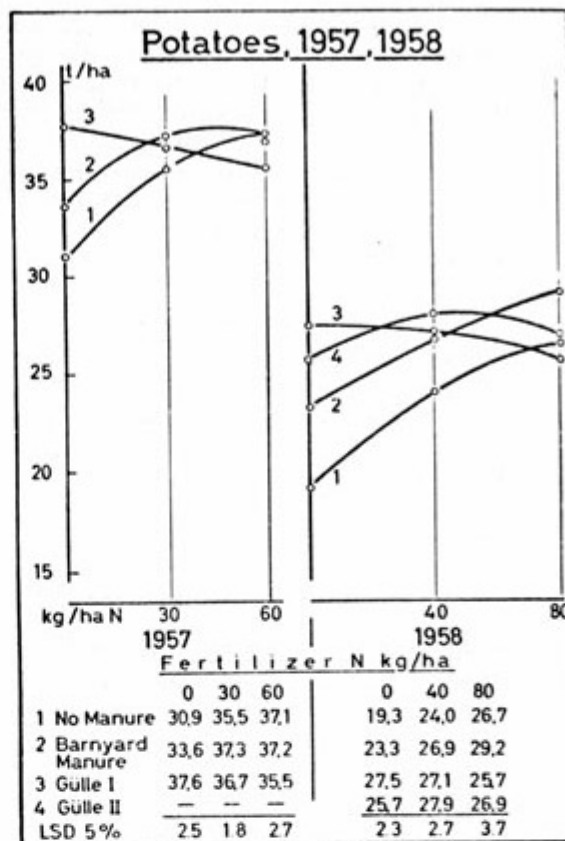
Fig. 45

Yields of potatoes with manures as shown in Fig. 44 arranged along yield curves with nitrogen fertilizer

In Figure 45, with reference to the same experiments, it is suggested that the curves obtained by variant 1, showing the yield increase by nitrogen fertilizer without application of animal manure, be elongated, thus presenting yield curves of the well-known shape with a descending part which can be obtained in an experiment by the application of progressive amounts of plant nutrients beyond the optimum quantity. The elongated curves accord well with the yield results obtained with the animal manures, thus demonstrating that the decreasing yields result from an oversupply of plant nutrients.

In these experiments equal quantities of fresh animal excreta and litter were compared after different treatment; the results can be taken as an evaluation of the treatment method. The conclusion is that liquid-manure exercises a higher effect on yield than solid manure, and that the quantities applied, together with fertilizers, should correlate well with the nutrient demand of the crop and the supply of the soil (Tietjen, 1966).

iii. Effect of feed additives on excreta as manure

Supplementing animal feed by antibiotics and other additives aims at increasing weight and feed conversion efficiency, and at maintaining or restoring animal health. A lasting effect on the excrement after defecation cannot be excluded. In the experiments of Elmund et al. (1971) the addition of antibiotics apparently altered the digestive processes in the digestive tract, resulting in faeces which were less biodegradable. As a consequence, supplementation of animal feed by high stability additives might need consideration when using animal manure for crop production.

In pot experiments with oats, a combination of fresh excreta from pigs and broilers was used, which had been collected during investigations on the nutritive effect of feed supplementation with carbadox, oleandomycin, oxytetracyclin, flavophospholipol, virginiamycin, zinc bacitracin, payzone and quindoxin. It was observed that crop growth could be hindered or enhanced as a result of interactions from increasing rates of nitrogen fertilizer. Carbadox remarkably increased dry matter production; higher nitrogen contents were related to flavophospholipol, oxytetracyclin and oleandomycin. Applying chlortetracyclin, zinc bacitracin and strepto-mycin to the soil did not affect the production of dry matter and the nitrogen content, but when they were applied with two varieties of chicken manure, dry matter production was decreased and the nitrogen content was increased to a remarkable extent.

Dietary supplementation by antibiotics and other kinds of additives may modify the biodegradation of excreta as well as its effect as manure on crop production (Tietjen, 1975).

iv. Normal and recommendable rate of manure application

The traditional type of farming with a balanced ratio of crop production and livestock husbandry in the same enterprise serves as the base for calculation. Knowledge and experience of the nutrient requirements of different crops are essential when deciding the amounts of manure to be applied. Nitrogen and phosphorus are considered the most important constituents as regards their effect on crop yield and environmental contamination. Recommended rates for manure are based on experience and research and they do not necessarily match the needs of crops, because only a little information is available on the annual rate of biological decay of organic materials. For this reason no certain predictions can be made about the availability of the organic bound nutrients.

NITROGEN UPTAKE BY OATS
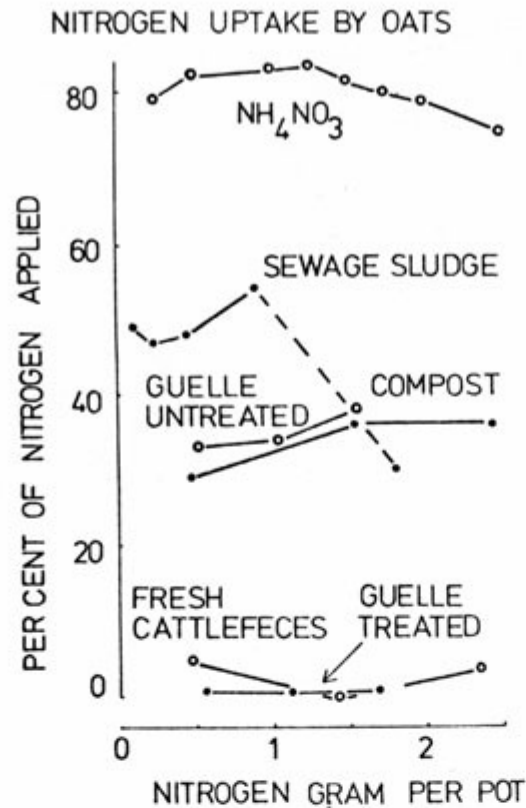
Fig. 46   Nitrogen uptake by oats as percent of nitrogen applied with
           increasing doses of 5 organic manure varieties and of NH_4NO_3

Recommended application rates are based mostly on the nitrogen
content and on its estimated available portion. Figure 46 demonstrates
by comparison of a few manures how great the differences can be between
the applied nitrogen and the nitrogen uptake by the crop. While about
80% of the nitrogen applied as NH_4NO_3 was taken up by oats in pot
experiments without loss by leaching, the portion was 30 to 50% with
pumpable sewage sludge, untreated cattle gülle and compost prepared
from battery hen droppings and peat. Nitrogen in fresh cattle faeces
and in cattle gülle treated by aeration was nearly unavailable in the first
period of growth; it is possible than there might be a longer and stronger
after-effect on the next crops, if no great losses occur.

Pratt et al. (1973) developed computer programmes to calculate
a number of manure decay series in combination with various rates and
times which demonstrate the nitrogen accumulating effect of annual
applications of manure varieties with a different availability coefficient.
This example is applicable to other nutrients, i.e. to phosphorus which
has a still lower availability, or even to heavy metals, whether trace
nutrients or predominantly toxic elements.

Every material that by its accumulation could be an environmental
hazard must be controlled, but its importance can be reduced by increasing
the availability or by narrowing the input-output ratio. Our proposal is to
match the nutrient supply to the need of the crops as closely as possible in
order to produce maximum yields with highest rates of uptake.
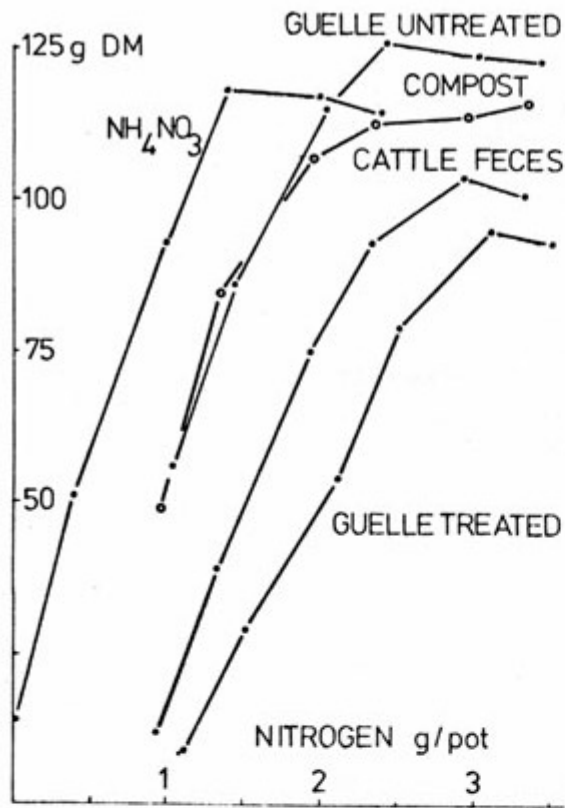
Fig. 47

Yields of oats as dry matter in pot experiments with four manure varieties (first marks, lowest yields) and increasing supplementary NH_4NO_3 rates
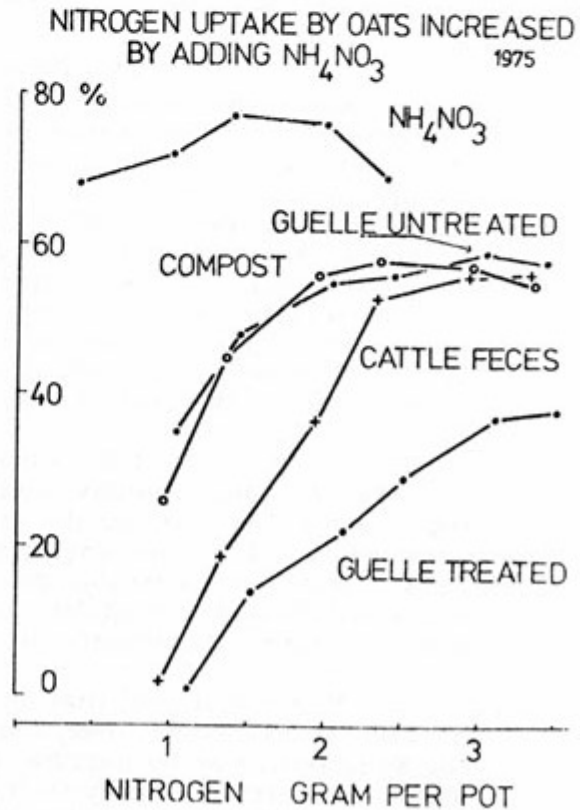
Fig. 48

Nitrogen uptake by oats as percent of nitrogen applied with four manure varieties (first marks, lowest values) and supplementary NH_4NO_3 rates

In Figure 47 the yield increasing effect of available nitrogen supplements to manure varieties is shown. Even the yields from fresh cattle faeces and treated cattle gülle are raised from a very low level to a better one by additional nitrogen application. This effect on the yield of crop mass can be transmitted to the input-output ratio of nitrogen, shown in Figure 48.

5.1.2 Night Soil

Since ancient times, mankind has used human excreta (so called night soil), cattle dung and compost, to maintain soil fertility. Night soil is richer in plant nutrients than cattle dung. In Graeco-Roman times, farmers used night soil to ameliorate the physical conditions of the soil and to recycle plant nutrients into it. In 1580, Bernard Palissy said: "For this you will understand why all excrement can help the generation of seeds. I say all excrement, either of man or beast." In Asian countries too such as China, Japan, India, etc., night soil was used as manure in ancient and mediaeval times. It is significant that for about the last two thousand years, Chinese farmers have maintained the productivity of their soils by very extensive use of night soil as fertilizer, although this raised the problem of controlling intestinal diseases. In view of the health hazards associated with the application of night soil as fertilizer, Japan reduced its usage after the second world war. However, if properly collected, stored and applied with all hygienic precautions, night soil is a most economic source of plant nutrients.

The chemical composition of night soil depends upon the diet, age and social status of the people producing it. Very recently Egawa (FAO, 1974, p. 266) reported the average composition of several Japanese samples of night soil as follows:

Table 15   CHEMICAL COMPOSITION OF NIGHT SOIL

Moisture	Organic Matter	Ash	N	P	K	NaCl
95%	3.4%	1.6%	0.57%	0.06%	0.22%	1.02%

Furthermore, the Handbook of Manures and Fertilizers (Jaiswal, 1971) describes the manurial values of human excreta as shown in Table 16.

Table 16   MANURIAL VALUE OF HUMAN EXCRETA
(% of original materials)

Manurial Constituent	Human Faeces	Human Urine
Moisture	75.0	97.0
Organic matter	22.1	2.0
Mineral matter	2.9	1.0
Nitrogen	1.5	0.6
Phosphorus	0.5	0.04
Calcium	0.7	0.2
Potassium	0.4	0.17
Organic carbon	11.0	0.8
C/N ratio	7.3	1.3

Garg et al. (1971) reported the possible availability of plant nutrients from human excreta per person per day in India as follows:

Particulars	Faeces g	Urine g
Quantity (natural condition)	133.00	1 200.00
Quantity (dry)	30.30	64.00
N	2.10	12.10
P	0.72	0.79
K	0.61	1.84

Night soil contains considerable amounts of salts and therefore it must be diluted before being applied to fields in order to avoid injury to plants by concentrated salts. Human urine is rich in urea; furthermore, it contains nitrogenous substances which become available to plants sooner than human faeces.

i. Collection and storage

It is absolutely essential that night soil be collected taking all hygienic precautions, such as protecting it from flies and the possibility of their breeding. It must never be allowed to pollute drinking water. In order to maintain proper sanitary conditions, automatic and well-covered latrines such as the "Wardha" and "water-seal" types (Jaiswal, 1971), suitable buckets and well-built tanks have been designed for the collection of night soil in different countries.

Human urine is collected in pits containing alternate layers of refuse and earth. Subsequently, the pit is covered with more earth and closed. After about two months, the material is ready for use as manure.

Night soil should be stored in well-built, covered or leak-proof tanks (or pits) which should either be shaded or underground. Even with good storage conditions, there is some loss of nitrogen from night soil as ammonia, formed from its proteinous material. In the event that night soil is kept under unfavourable conditions, such as exposure to sun or wind, these losses may be very significant. In order to minimize the loss of nitrogen from night soil, 3-5% superphosphate is added to it during storage. The loss of plant nutrients from night soil is likely to be less if human urine and faeces are stored together rather than separately.

Night soil must be kept for 3-4 months before applying it to the fields. It is believed that within several weeks of storage, pathogenic bacteria and protozoan parasites are destroyed and that during the period of 3-4 months, ascaris and hookworm eggs are either destroyed or become attenuated. As mentioned, in order to avoid injury to plants by concentrated salts, night soil must be diluted with 2-3 times as much water before use. To have a regular supply of well-fermented and ripened night soil, it is desirable to store it in a number of tanks filled in turn at different periods. The night soil should then be used from them in rotation.

ii. Methods of application for plant nutrition

Night soil is applied to soils for plant nutrition mainly in the following ways:

a. direct application
b. as compost
c. as a source of sewage and sludge.

a. Direct application

After dilution and proper ripening or storage, night soil is applied directly to the soil and it is most important that it is then covered with soil to prevent any foul smell or fly problem as well as loss of ammonia.

b. Night soil compost

A significant method of using night soil as manure is after composting with other organic materials, such as town refuse, cattle manure, household rubbish, etc. However, proper hygienic precautions must be taken when handling night soil during the process of composting in order to check the incidence of faeces borne diseases. Chinese workers observed that when composting night soil with rice straw, there is a temperature increase for a sufficient period of time to destroy ascaris eggs completely and to control fly breeding to some degree. Furthermore, there was no significant loss of nitrogen during composting. They obtained similar results by composting cattle manure with night soil.

It has been reported that aerobic methods of composting with night soil are quicker and that bad smells are not produced. Therefore, the consensus is that the aerobic methods are better than anaerobic to produce compost from night soil. It need hardly be emphasized that by composting night soil with city refuse, household garbage, industrial waste, etc., not only are useful manures obtained but the problem of city sanitation is also partially solved.

As described previously, urine properly stored on alternate layers of earth and refuse can later be applied as manure.

A substance called "poudrette" has been prepared from night soil by mixing and dehydrating it with absorbing materials such as charcoal, sawdust, ashes, earth, etc., but there are conflicting reports in the literature regarding its utility as manure from the hygienic as well as the economic points of view. According to one report, they are highly inefficient as manure because considerable amounts of nitrogen are lost during the process of drying.

c. Night soil as a source of sewage and sludge

Night soil is also a source of sewage and sludge. In the developed countries and in most of the big cities of the developing countries, there are underground sewage systems to collect human excreta mixed with washwater. In these sewage systems human faeces and urine are collected by mixing them with a large amount of water; this sewage consisting of soluble as well as solid materials, mostly in colloidal form, is led into underground sewers. Subsequently it may be purified and then allowed to flow into rivers or the sea. Alternatively, as sewage is rich in plant nutrients, it may either by used as manure or sludge may be prepared from it. However, a number of problems are associated with the use of sewage and sludge as manure in agriculture. The details of sewage and sludge as manures are given elsewhere in this bulletin.

iii.   Economic aspects of the use of night soil as manure and further research needed

Night soil has a rich potential value as manure, especially for the developing countries. For instance, according to one estimate, the amounts of plant nutrients shown in Table 17 could be available from night soil per year in India (Jaiswal, 1971).

Table 17   TOTAL N, P AND K EXCRETED ANNUALLY BY THE ENTIRE POPULATION

Item	N	P	K
	million tons		
Human faeces	0.383	0.132	0.110
Human urine	2.207	0.140	0.335
Total	2.590	0.270	0.445
or say	2.6	0.27	0.45

Value as calculated by van Voorhoeve (1974):

Approx. value (million US $)	520	155	35

Total value: 710 million US $)

Regarding the use of night soil as fertilizers, Duncan (1975) suggests: "It is probable, however, that the least social cost systems will be rather labour-intensive, using little capital and providing employment." Therefore, the large scale use of night soil as manure is highly suitable for the developing countries. However, in order to achieve this, proper sanitary precautions have to be taken; infrastructure has to be built for its collection, storage, and application; and extension work has to be organized on a massive scale to propagate the use of night soil as fertilizers as in certain cases there may be a psychological bias against it.

Intensive research should be carried out on the influence of the application of night soil on the physical, mechanical and chemical properties of soils, such as carbon and nitrogen contents, C/N ratio (organic as well as mineralized N), base exchange capacity, pH, conductivity (salt concentration), buffering capacity, porosity, sticky point, hydraulic conductivity, etc. and on different types of soils under different climatic conditions. In addition, research is also needed to develop efficient, hygienic and economic methods of collection, storage and application of night soil to the land.

5.1.3 Peat

The amount of peat in the world in given in Table 18. Most areas of peat are located in the humid and moderate climatic zone, although its formation is possible in tropical climates, e.g. in Israel (Hula peat) and Indonesia. The peat areas in the tropics are not sufficiently well-known. The possible use of these resources to ameliorate tropical soils was demonstrated by Zohar (1975) with desert soils in Israel.

Table 18   DISTRIBUTION OF PEATLANDS IN VARIOUS COUNTRIES
(according to Schneider, 1976)

Country	Peat land in km²=100 ha	Peat land in % of area of country	Country	Peat land in km²=100 ha	Peat land in % of area of country
Europe			Asia		
Finland	100 000	32.0	USSR -		
Sweden	55 000	14.5	Asiatic part	414 000	3.7
Norway	30 000	9.2	Indonesia	15 644	-
United Kingdom	15 819	6.6	Borneo Sarawak	14 660	2.1
Scotland	8 214	10.7	Brunei	984	-
England	3 617	2.8	Sumatra	-	-
Northern Ireland	2 400	17.8	Japan	2 000	0.6
Wales	1 588	7.5	Israel	50	0.2
Poland	15 000	4.8	Bangladesh	-	-
Ireland	12 000	17.1	China	-	-
Federal Republic			Korea	-	-
of Germany	11 250	4.5			
Iceland	10 000	9.7	Africa		
German Democratic					
Republic	4 890	4.5	Ruanda	-	-
Italy	1 200	0.4	Tanzania	-	-
France	1 200	0.2	Zaire	-	-
Denmark	1 000	2.3			
Hungary	1 000	1.1	America		
Netherlands	450	1.3			
Czechoslovakia	330	0.3	Canada	100 000	1.0
Austria	220	0.3	USA without Alaska		
Yugoslavia	150	-	and Hawaii	75 000	1.0
Romania	70	-	Cuba	4 500	3.9
Spain	60	0.6	Uruguay	1 000	0.6
Switzerland	55	0.1	Argentina	450	-
Greece	50	-	Bolivia	-	-
Belgium	10	-	Brazil	-	-
Bulgaria	10	-	Chile	-	-
			Australasia		
USSR -			New Zealand	1 670	1.5
European part	301 000	-	Tasmania	-	-

The most important moor types are conditioned by their formation:

high moor   - the water regime depends mainly on rainfall, therefore the nutrient state is low. The plants are chiefly sphagnum and eriophorum;

transition moor - is the zone built up between high and low moor. The vegetation is composed of carex, phragmites and trees such as pine, birch and alder;

low moor   - is formed under surface and groundwater influence, the plant species are carex and phragmites.

High moor peat is acid and poor in nitrogen and other nutrients, whereas low moor peat is generally neutral and high in lime, nitrogen and other nutrients.

According to Baden (1972) peatlands can only be used for agriculture by:
i) cultivation without application of mineral material or by using them as grassland, or ii) cultivation after deep ploughing (till 1-2 m depth) and mixing the subsoil material (sand) with the peat, the profile under the cultivation layer showing alternatively sloping layers of peat and mineral material. The land can be used for cultivated and sod crops. Good drainage is also necessary if peatlands are to be used for agriculture. The high water-holding capacity of peat ensures a sufficient water supply.

The fertility of peat lands depends, as in mineral soils, on the availability of nutrients and the pH (Hupkens van der Elst, 1972; Kurki, 1972; Rayment 1972).

High moor peat (undecomposed or slowly decomposed) is cut from the natural site and used as an organic additive, usually in intensive horticulture. Its main action is to improve physical soil conditions and Puustjärvi (1963) observed an improvement in the water and air regime of soil after application of peat. However, it is not only the physical properties of peat that influence its action after application, but also its chemical composition and decomposition products can exert a direct influence on the growing plant.[1] It has even been used as an additive to feedstuffs for animal nutrition.

The production and transport expenses of the loose, voluminous peat material make it necessary to consider the cost benefit ratio. Thus, generally, the use of peat would be justified in horticulture, especially for greenhouse culture. Puustjärvi (1975) established that "at the moment moss peat is commonly considered the best available growing medium for intensive greenhouse culture."

Investigations have been made about defined compounds such as phenols, amino acids, aliphatic acids and some others which can be isolated from peat (Nauke et al., 1972, Söchtig, 1974; and Maciak, 1971). It would be interesting, especially in countries where there is a high decomposition rate of peat because of the climate, to see how far plant growth is increased by concurrent formation of substances of the groups mentioned and if they contribute to the economics of horticulture.

5.2 SOLID AND LIQUID WASTES

5.2.1 Definitions

How should waste be defined? Numerous proposals have been made. Different points of view and aspects give rise to different types of classification. Livestock manure, for example, cannot be regarded as waste when spread upon land in a regular cycle of crop production; but livestock excrement is regarded as waste when produced as an inconvenient, even noxious, by-product of animal husbandry in concentrated livestock and poultry operations and in feedlots which are grouped as point sources of pollution because they operate without crop land and crop production.

Waste can be classified according to:

- its origin: domestic, commercial, industrial, etc.;
- the method of collection and transportation: household standard container, bulky refuse, public or private collection, etc.;

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[1] Christeva et al., 1972; Tolpa, 1972; Söchtig and Harms, 1971; Flaig and Söchtig, 1972.

- its composition: liquid, solid, combustible or
  non-combustible;
- compostable or non-compostable;
- public health aspects: hazardous, toxic or not
  (Schenkel, 1973).

A terminological classification is proposed by Brink (1973):

a. Processes for handling waste

Waste handling	- cleansing	
	- treatment	
	- depositing	

Cleansing	- collection	
	- sorting	
	- transport	

Treatment	- depositing	- piling
		- storing
	- emission	- spreading
		- leakage
	- recuperation	- re-use
		- extraction

b. Equipment for handling waste

   Plant
   Plant subsection
   Specialized equipment

c.

Types of waste		Example
Natural	:	forest
Industrial (factory)	:	excavation
Municipal or urban	:	household
Production	:	animal
		chemical
		excrement
		fuel
		mineral
		mining
		nuclear
		plant residue
		pharmaceutical
		photographic
		etc.

These classification proposals have been developed according to the aspect of waste handling: collection, transportation, treatment and final disposal. These aspects prevail mainly for public health reasons, in densely populated communities with a high level of industrialization. The aspects of re-use, reclamation and recycling of organic wastes as fertilizers will need revised policies in order that wastes are:

- viewed as a resource,
- considered an integral part of regular crop production,
- free from toxic quantities of disadvantageous
  ingredients, and
- consistently available at the right time and place.

It would be useful if wastes could be separated at the beginning of collection to exclude undesirable and disadvantageous wastes, thus raising the value of the remaining recyclable materials.

5.2.2 Properties of Solid Waste, Wastewater and Sewage Sludge

The term "solid waste" means garbage, refuse and other discarded solid materials resulting from industrial, commercial and agricultural operations, and from community activities. In municipal wastes the proportion of industrial and agricultural materials is smaller than domestic and commercial wastes which predominate. "Hazardous wastes" that present a significant hazard to human health and the environment must be excluded from biological recycling procedures.

Used water from individual sources in the community is collected and transported by municipal wastewater systems through sewers to some dumping point. Normally sanitary and industrial waters are included, also urban runoff from streets, etc., and sometimes agricultural wastes. Industrial wastes should be excluded if they present a health hazard to operators in sewage treatment plants, or if they are corrosive to parts of the facilities, or if the pollution load of the effluent is still too high for discharge into a watercourse. After primary, secondary or tertiary treatment, wastewater is transformed into two new constituents: effluent and sludge.

The liquid product of treatment is effluent and its final disposal is relatively easy; it is discharged into a watercourse, often with little attention paid to the usual accompanying problems of water pollution or eutrophication, or it is applied in some way to the land to re-enter the water cycle with a minimum disruption of nature.

Sludge is the solid residue of the wastewater purification process, a product of screening, sedimentation, filtering, pressing, bacterial digestion, chemical precipitation and oxidation. Sludge is not so easily disposed of as effluent. The more steps in treatment, the more efficient the process of purification, the greater is the volume of solid produced. Handling such quantities of sludge solids is expensive.

5.2.3 Criteria for Decisions in Waste Management

In the effort to develop and operate waste management programmes, decisions must be made which are essentially determined by four basic criteria: costs, environmental factors, resource conservation and institutional factors (Colonna, 1976). Each category includes the following key points:

Costs

Operating and maintenance
Capital

Environmental factors

Water pollution
Air pollution
Other health factors
Aesthetic consideration

Resource conservation

Energy
Materials
Land

Institutional factors

Political feasibility
Legislative constraints
Administrative simplicity

Normally, cost criteria are the most important, but often institutional factors are of major concern since they can prevent a decision from being made or eliminate an alternative. As communities are becoming increasingly conscious of the need to conserve resources, this criteria is gaining in importance. But to quantify it is difficult as long as there is no distinctly fixed goal. This will be different as soon as wastes are considered as 'resources out of place' and that a good portion of the constituents could exercise a beneficial effect on the soil and on crop growth.

5.2.4 Land Disposal or Reutilization for Crop Production and Soil Conservation

The decision to rank 'resource conservation' in first place necessitates that some technique of land use be designed which is different from the more usual land disposal. Although to return waste into the natural cycle of transformation by land application implies final waste disposal at the same time, both land disposal and land application must be considered as alternatives. The design and operation of facilities classed as land treatment must take into consideration and accommodate the qualities both of the natural conditions of the site and the applied waste which is utilized to produce crops. This often requires some pretreatment and considerable capital investment (Hartman, 1975).

Solid waste consists of organic and inorganic materials, biodegradables and non-biodegradables or non-compostables. Removal of some of the latter is often necessary in order to upgrade the quality of the compost. Furthermore, to ensure a sufficiently rapid, and hence economic, processing time, there must be some form of particle size reduction, separation by handpicking, screening and magnetic separators adjusted to the technology of composting in windrows, in a digester, or in a bin, tank or drum.

Wastewater destined to provide fertilizer and irrigation for the production of food and the restoration of greenery requires pretreatment to remove constituents that are toxic to crops or present a health hazard to man or beast. It is important to distinguish between disposal and reutilization; designers of land treatment systems have different purposes in mind: the goal of maximum disposal may be mutually exclusive with the goal of maximum reutilization.

An example is given by Stevens (1972): at Seabrook Farms, New Jersey, USA, a food processing plant must handle 45 000 m^3 wastewater per day on 80 ha (20.5 m per year). Because of the fortuitous soil and climatic conditions, this can be done by spraying the daily output directly on to 34 ha of land (132 mm per application). This procedure does not achieve the maximum irrigation potential but it does accomplish the design goal of disposing of 45 000 m^3 without polluting the local watercourses. On the other hand, the municipal facility at Muskegon, Michigan, USA, is designed to handle 163 000 m^3 per day. To give an economic benefit to the county it serves, 2 500 ha of relatively infertile land have been selected for spray irrigation to stimulate crop production and agriculture (2.4 m per year in height). Another example that can be mentioned has an even more decreased load: the Sewage Utilization Association of Braunschweig, Germany (F.R.), handles about 33 000 m^3 per day by spray irrigation on 4 000 ha of cropland, which is an area nearly the same size as Muskegon, but the load of 350 mm per year is only one seventh. It corresponds with the average water deficit in the main growing period from spring to autumn at this site, Figure 49 (Tietjen, 1975b). A new, thorough survey in 1976 recommends this well-balanced biologically based wastewater recycling system as a model worth imitating (Bath, 1976).
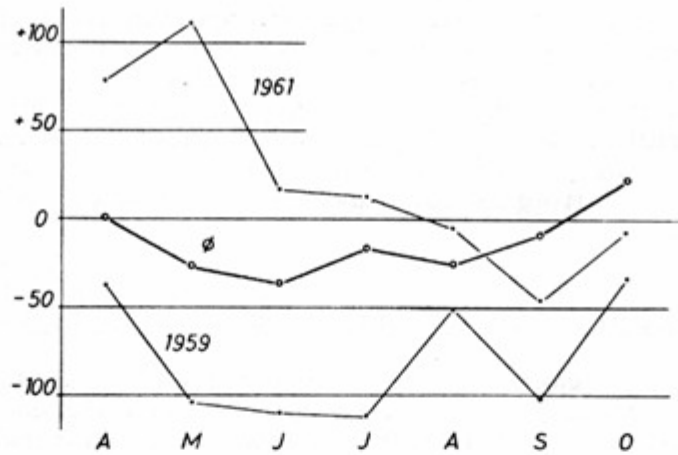
Fig. 49   Climatic water balance at the site of the
Sewage Utilization Association of Braunschweig

5.2.5   Composts from Solid Waste: Quality Criteria

Municipal refuse compost is used in all crop growing and soil amelioration areas, i.e. crop and grassland farming, horticulture (fruit, flowers and vegetables), viticulture, as well as in tree-nurseries, forestry, reafforestation, land reclamation and various types of landscaping.

The Netherlands provides an outstanding example of compost production and use over many years (they also rank first in the world consumption rate of mineral fertilizer). Table 19 gives a survey of compost production in this country from 1959 to 1971; it also shows the main areas using compost and their changing proportions (Vam, 1972).

Table 19   CHANGE IN COMPOST USE IN HOLLAND

Area of use	1959 %	1963 %	1967 %	1971 %
Crop and grassland	48	22	9	0
Chicken and pig husbandry	2	1	2	4
Fruit culture, vegetables, flower bulbs	25	47	40	16
Forests	3	0	0	0
Landscaping, recreation areas	22	30	49	80
Total production, t	194 300	205 600	182 700	
Vam-production, t		154 600	162 800	138 550

The different requirements of crops and trees, flowers and vegetables, etc. for best growth cannot be supplied by the same compost. While the crop needs vary greatly, so also does the composition of the compost, owing to

differences in type or combinations of types of material being composted. Thus, if necessary, the compost can be adjusted or fortified by additives according to the specific demands of crops (Golueke, 1973).

The three most important requirements concerning compost quality are:

- absence of substances injurious to man, crop or soil;
- high content of organic matter and plant nutrients;
- low content of useless substances like stones, slag, fragments, plastic, etc.

Additional sorting and sieving are necessary to lower the content of useless substances, thus increasing production costs for special grades of compost. Therefore it is wise to make cost saving gradations according to the purpose of application. For instance, quality requirements are lower for waste land reclamation and reafforestation areas than for woodland areas; they are higher for viticulture and fruit culture, still higher for agriculture, and highest of all for vegetable growing in gardens and pasture farming. Several quality and price gradations can be considered; i.e. for inexpensively produced compost to be used on wasteland that is being reafforested, and for better grades of compost, free of glass and metal splinters, that may be used on pastures and in gardens.

Different grades of compost are produced according to the particular processes used. The original product might be shredded or ground refuse, 'raw compost', with a high content of easily decomposable organic matter, beneficial for mulching purposes. After treatment in a digester for some days, this product might be called 'fresh compost'. Usually, the hygiene tests show that this product is already free of pathogenic organisms. When fresh compost is stored in windrows for a longer period organic matter gradually breaks down. Heat energy usually accumulates and the temperature of the mass remains high until the readily decomposable material has been broken down. At that point bacterial activity begins to decline and the temperature drops (Golueke, 1973). The product is called 'rotted compost'.

Raw, fresh and rotted compost are gradations according to the process of decomposition. More variation is caused by the type of material being composted. This shows that a general standardization of compost according to the content of physiologically efficient ingredients is impossible. Furthermore, living conditions and habits in a community change constantly and the composition of waste changes correspondingly. Figure 50 demonstrates the steady increase of organic matter in fresh compost after treatment in a Dano drum and in rotted compost after storing in windrows at Bad Kreuznach from 1959 to 1973.
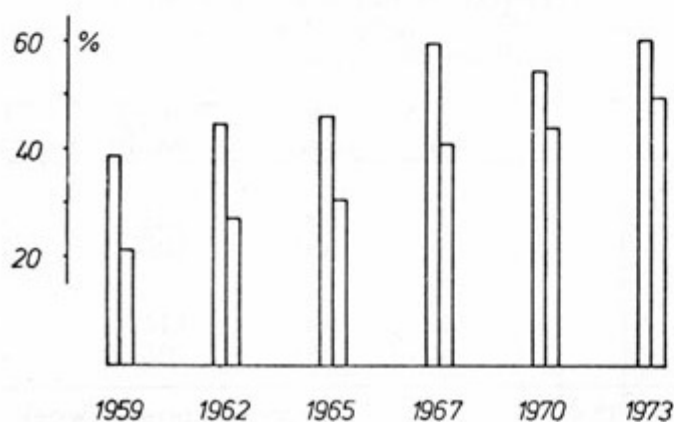
Fig. 50

Organic matter content in municipal refuse compost (% in dry matter) Bad Kreuznach 1959 - 1973 Fresh compost (1 week): left columns; rotted compost (6-9 months): right columns

Evaluation as a fertilizer

A comparison of stable manure and municipal compost (Table 20, Kick, 1971) shows a low content of plant available nutrients in the compost. In order to achieve high crop yields, compost applications must be complemented by quick-acting fertilizers. The contents of trace elements in compost (i.e. Cu, Zn, Mn, Mo, B) is ten to a hundred times higher than in stable manure, so the application of very great quantities of compost could be injurious to crop growth.

Table 20 COMPARISON OF STABLE MANURE AND MUNICIPAL COMPOST

	Manure	Compost
	kg in 10 t	
Yield effective in the first year:		
N	15 – 20	8 – 10
P	7 – 9	4
K	50 – 58	25 – 33
Alkalinity (CaO)	60	500 – 1 000
Organic matter	1 800	900 – 1 500
Total:		
Mg	6 – 12	24 – 30
Na	15	30 – 37
S	20 – 30	50 – 300
Cu	0.02	0.8 – 1.2
Zn	0.12	8 – 12
Mn	0.4	4 – 6
Mo	0.001	0.1
B	0.03 – 0.04	0.6 – 3.6

Table 21 demonstrates how the yield increase due to compost depends on a balanced ratio of nutrients and on the general yield level that is given by the natural fertility of the soil or by the use of fertilizer. A yield increase of 23 - 26% on the lowest yield level was achieved by compost, but was affected by lack of nitrogen and phosphorus. With both these nutrients added as quick-acting fertilizers the yield level was raised by 70% and the relative calculable yield increase by compost reduced to 4%.

Table 21 YIELD INCREASE BY MUNICIPAL COMPOST
(1959 to 1973 average for potatoes, rye and oats
dry matter with five compost applications
totalling 480 t/ha)

Compost	None dt/ha year	Rotted relative values	Fresh
No P fertilizer:			
No N fertilizer	37.9 = 100	123	126
With N fertilizer	59.7 = 100	106	109
With P fertilizer:			
No N fertilizer	42.5 = 100	114	118
With N fertilizer	61.7 = 100	104	104
Rotted compost 6 to 9 months		Fresh compost 1 week	

ii. Evaluation as a soil conditioner

Use of compost in the context of good humus husbandry effects crop growth and yield indirectly by conserving and improving the soil. Compost promotes soil aggregation and stabilizes soil structure. This improves the air-water relationship of soil, thus increasing the water retention capacity and encouraging more extensive development of plant root systems (Golueke, 1973). Figure 51 is an example of the long-lasting effect of compost application on the water holding capacity. The differences shown in the figure were caused by a single compost application; they are of great importance in the experimental area which has an annual rainfall of less than twenty inches (Banse, 1961).
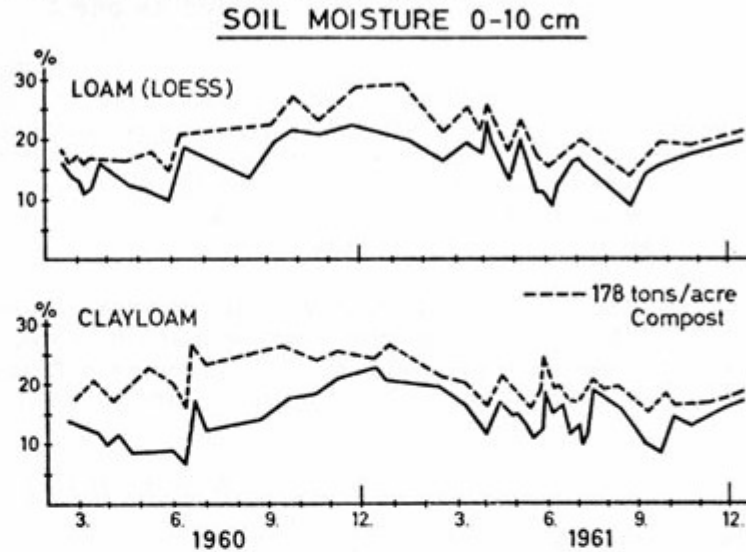
Fig. 51

Lasting effect of compost application on soil moisture content

Improved soil structure counteracts soil erosion. Figure 52 shows the soil conserving effect of composts in a vineyard with plots arranged for measuring erosion and runoff during short but heavy rainfall. The compost applied in great quantity to one plot twelve months before the storm almost completely prevented runoff (Bosse, 1969).
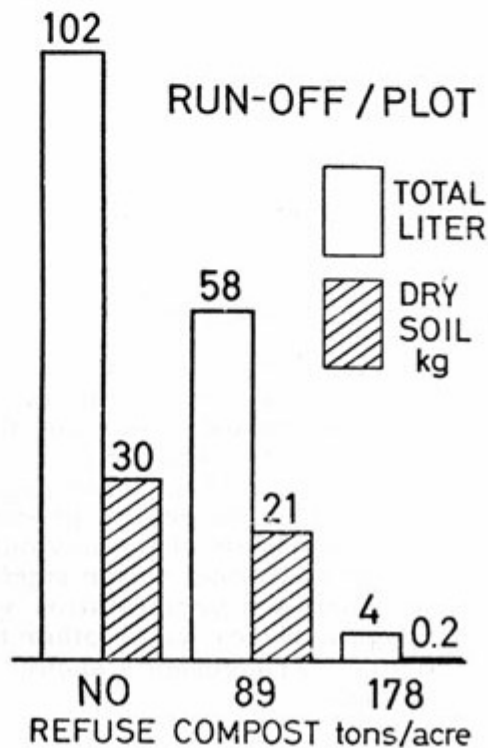
Fig. 52

Decrease of soil erosion in a vineyard by adding compost (slope 58%, plot 24 m^2)

5.2.6   Land Application of Wastewater

      Municipal wastewater contains suspended and dissolved solids, organic and inorganic substances. In purification processes by primary and secondary treatment, mechanical and biological, these substances can only be partially removed. Even after secondary treatment, wastewater from a community may still contain levels of pollution damaging to the receiving stream. To meet this problem, methods of advanced wastewater treatment are available. They are regarded as tertiary additions to the secondary treatment facilities.

      Application of wastewater to land is classed as an advanced method of treatment with an extremely high purifying effect. Properly designed and operated, land treatment is regarded as one of the most innovative techniques available for wastewater treatment (Stevens, 1972; Hartman, 1975). Wastewater applied to cropland is not only purified, but the ingredients in it are also utilized. Plant growth, as a biological medium of treatment, may be regarded as a significant element for long lasting efficiency in controlled land treatment facilities. Some systems require primary or secondary treatment prior to application to the land. This pretreatment is often provided, not out of consideration for the limits of the soil and plant filter, but as a consequence of legal requirements for wastewater treatment (Stevens, 1972).

      Municipal wastewater characteristics are listed in Table 22 (Pound et al., 1973) for untreated sewage and for water applied to land. Evidently, the pretreatment removed some organic substances and reduced the values for BOD and COD. This is considered unnecessary if applied to land (Loehr, 1975).

Table 22   MUNICIPAL WASTEWATER CHARACTERISTICS

Constituent	Untreated sewage mg/l	Actual quality applied to land mg/l
Total solids	700	760 - 1 200
BOD	200	10 - 42
COD	500	30 - 80
N	40	10 - 60
P	10	10 - 25
B		0 - 1.0
Na		190 - 250
K		10 - 40
Ca		20 - 120
Mg		10 - 50

i.   Climate, soil and groundwater

      When the decision is made to apply wastewater to land for crop production, a few dominating criteria determine the details of site selection, design and, later on, the operation (Hartman, 1975). Wastewater is above all a source of water supply, so where there is no need for water, no success in crop production will be achieved by wastewater land treatment. The growth promoting substances in wastewater can reach their maximum efficiency only in conjunction with the beneficial effect of the additional water supply. The climatic water balance, the difference between precipitation and evaporation, can be used to estimate the average need for water other than the rainfall. During humid and cold periods arrangements should be made to store the wastewater, e.g. in ponds.

Soil is another important factor in wastewater land treatment. Infiltration and percolation rates must be thoroughly surveyed to prevent soil clogging by incorrect wastewater application techniques.

Attention must be paid to the depth of the groundwater table. It is expected that when wastewater is applied to the land with the primary goal of crop production, the applied water and its ingredients will be utilized entirely by the crop. There is, at least in the beginning, no intention to recharge groundwater. Wells and drains can be employed to ensure that the groundwater level remains constant below the drainage system which prevents the applied wastewater from percolating down to the water table. Quality standards can be safeguarded by monitoring of treated effluent.

ii.   Rates and methods of application

Each proposal for land treatment is approached as a unique combination of natural systems, to be evaluated in connection with the goals of the wastewater processor. A thorough survey of soil, climate, hydrology and the vegetative cover must be made. There are different approaches to land application and the three most important are irrigation, overland flow and infiltration-percolation (Pound, 1973). Table 23 lists their characteristics for comparison; for instance, under 'Irrigation', spray or surface is the only approach, classified as 'excellent', adjusted to crop production. In comparison with the other methods, 'Irrigation' has the smallest application rate, needs the largest area, has a soil of good productivity but it does not exclude the possibility of influencing groundwater quality with an annual application rate of 2-8 ft and a depth to the groundwater table of about 5 ft.

Table 23   COMPARATIVE CHARACTERISTICS OF WASTEWATER
LAND APPLICATION APPROACHES
(Thomas and Harlin, 1972, quoted by Pound et al., 1973)

Factor	Irrigation	Overland flow	Infiltration-percolation
Annual application	2 to 8 ft	8 to 24 ft	18 to 500 ft
Land required for 1-mgd flow	140 to 560 acres plus buffer zones	46 to 140 acres plus buffer zones	2 to 62 acres plus buffer zones
Application techniques	spray or surface	usually spray	usually surface
Soils	moderately permeable with good productivity	slowly permeable clay loams and clay	rapidly permeable sands and sandy loams
Probability of influencing groundwater quality	moderate	slight	certain
Needed depth to groundwater	about 5 ft	undetermined	about 15 ft
Use to grow crops	excellent	fair	poor
Use in cold climates	fair	-	excellent

5.2.7 Sewage Sludge

The normal purpose of a sewage treatment plant is to receive the collected and sewer-transmitted wastewater, purify it and then dump it into waterways which are often already burdened by other waste disposal facilities. The higher the purification efficiency of the treatment procedure, the greater is the quantity of retained sludge to be treated and removed for final disposal. There are many procedures available for intermediary treatment to change the mass and volume of the sludge, but there are only two alternatives for its ultimate removal - land or ocean dumping on the one hand, and delivery to agriculture for spreading on cropland on the other hand, Figure 53 (Möller, 1971). Pyrolysis may become the third alternative, although requiring the use of sunstantial quantities of auxiliary fuels (Colonna, 1976).
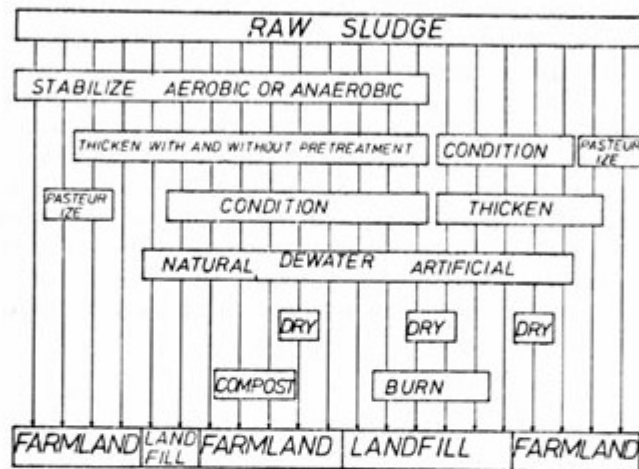
Fig. 53   Scheme of sludge treatment procedures

i.   Evaluation as a fertilizer

Sludge is used on cropland in a liquid, sticky or crumbly state, the first being the most popular form today. The manuring effect of sewage sludge is good, although different from that of rotted animal manure. The latter is simpler to use as the nutrients are well balanced and their availability in the soil for plant nutrition proceeds slowly, according to the progress of decomposition and transformation. In sewage sludge the ratio of nutrients is unbalanced and the variation is great (Fig. 54); there is usually a deficiency in potassium and a greater portion of the total nitrogen content is available at once, Table 24. However, the yield efficiency of sludge nitrogen is even lower than that of nitrogen in ammonium nitrate, Figure 55. These differences from stable manure and inorganic fertilizer must be taken into consideration in order to obtain maximum effects. Balancing the ratio of nutrients in sludge by applying potassium to offset the additional nitrogen distinctly increases the crop yield; there is a more complex uptake and better utilization of the applied nutrients, thus decreasing any possible pollution potential in run-off or leachate (Figs. 56 and 57).
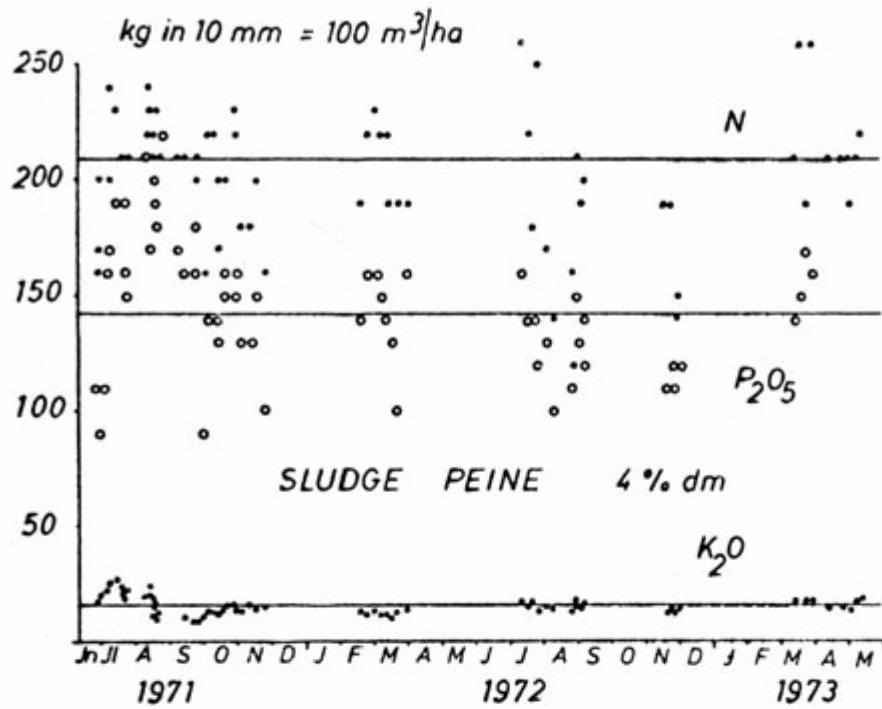
Fig. 54   Variations over two years in plant nutrient contents
of sewage sludge from the city of Peine

Table 24   MUNICIPAL SEWAGE SLUDGE CHARACTERISTICS
Example: City of Peine, activated sludge, 69 samples
1971 to 1973

Constituent	kg in 10 mm = 100 m³/ha
Total solids	4 100
Ignition loss	2 100
N	210
P	60
K	13
Na	11
Ca	200
Mg	15
Fe	120
Cu	1.4
Pb	0.1
Ni	0.6
Zn	5.1
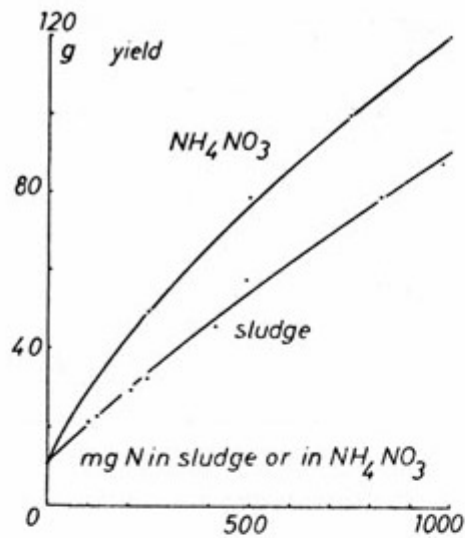
Fig. 55   Yield effect of nitrogen in sewage sludge and in
NH_4NO_3 in a pot experiment with oats
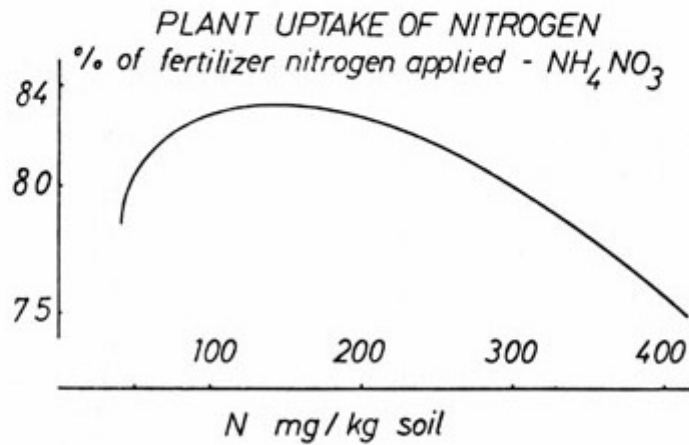
Fig. 56   Uptake of nitrogen by oats (grain and straw) in
pot experiments, average of 11 years
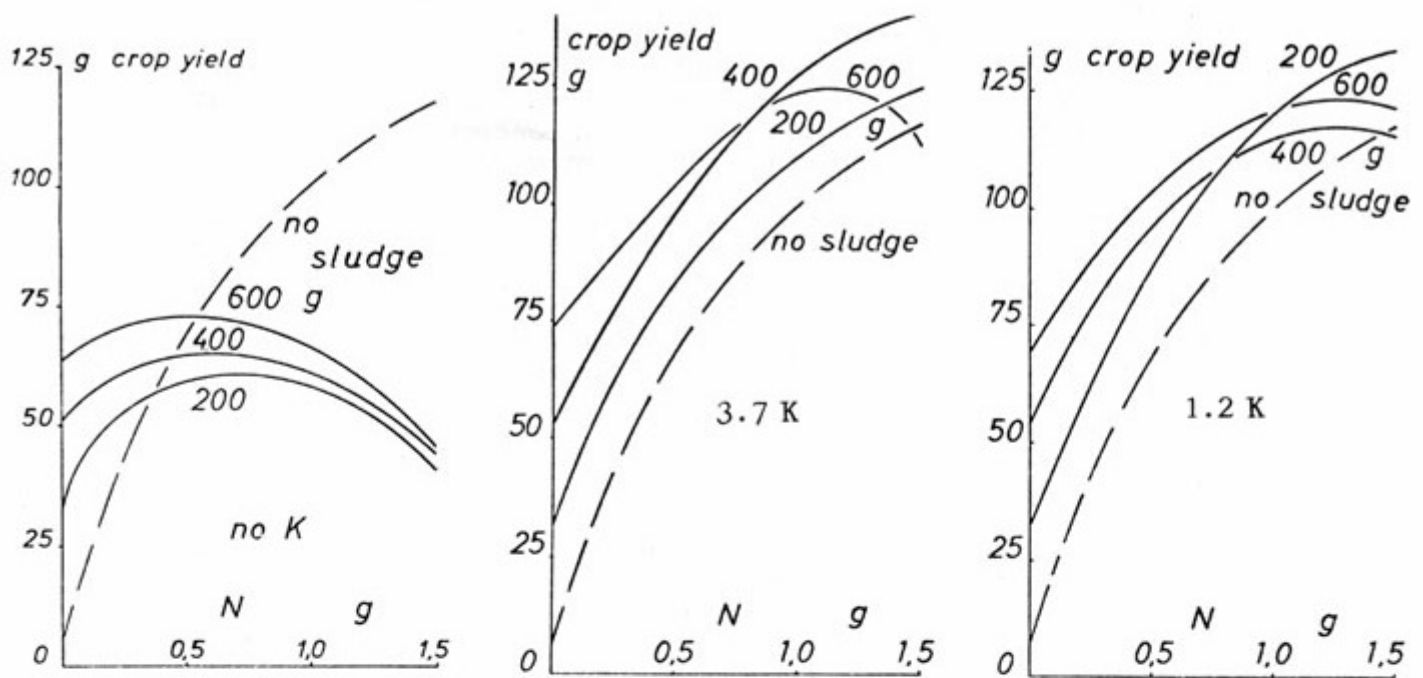
Fig. 57   Effect of potassium on balance and utilization of
nutrients in sewage sludge

ii.   High-rates of application

     The application of sludge in amounts surpassing the nutritive
demand of the crop means enriching the soil with nutrients and raising
the fertility level, usually with a lasting effect on the increase in crop
yield. This procedure can only be used if it does not damage the crop
and will not contaminate groundwater. High-rates of sludge application
are feasible by applying small amounts of sludge at short intervals,
adjusted to sludgewater infiltration and evaporation, combined with a
cultivation that mixes and aerates the soil so that moisture and air are
kept in good balance (Tietjen, 1973).

     In a field experiment on loamy sand, 10, 93 and 366 mm of
municipal sludge were sprayed at a rate of 10 mm a time over several
months. The nitrogen content of the soil, soil water and the crop (kale
and sugar beet) were influenced only to a very small degree by 10 mm
of sludge; 366 mm of sludge increased the ammonia content in the upper
soil layer for three months after fianl application. Soil water collected
by suction cells at depths of 1 and 2 m was enriched with nitrate up to
600 ppm for a long period of observation. Thus sludge application in
large quantities must be restricted to sites with a great depth to the
groundwater table and slowly permeable soil (El-Bassam, 1974).

5.2.8 Predominantly Toxic Compounds

Solid and liquid municipal wastes contain not only essential or useful plant nutrients, but also toxic or noxious compounds. When waste is delivered to farmers for use on cropland, it should be an inevitable condition that the waste is unobjectionable for crop production; i.e., the contents of toxic and noxious compounds must be very low compared to the essential nutrients. Application rates should be limited only by high concentrations of nutrients, never by concentrations of predominant toxic or noxious compounds.

The most important sources for these unwelcome substances are industrial waste and wastewater. If it is impossible to exclude these wastes from the public collection system and from being mixed with harmless municipal waste, special attention must be given to those pretreated wastes which are delivered for land application and crop production. Reliable analyses are necessary in order to calculate the permissible application rate.

Crops are not good indicators of the presence of higher amounts of predominantly toxic substances. With regard to growth and yield, crops can tolerate much higher levels of toxic substances than are permitted in eventual foodstuffs.

Knowledge of those substances in waste that are not nutrients and about their behaviour in soil in still incomplete. Most of them, especially heavy metals, are found to accumulate in the upper layer of the soil (El-Bassam, 1975). Thus no groundwater contamination will occur, but the continuing enrichment in the root zone must be controlled. We do not know enough about the level at which crops will be damaged under different soil conditions, so the list of 'Tolerable Amounts' shown in Table 25 must be accepted preliminarily as a proposal.

Table 25 TOLERABLE AMOUNTS OF SOME ELEMENTS IN SOILS REGARDING THEIR PLANT COMPATIBILITY

	Range		Total amounts ppm	
			Most frequent	Tolerable (proposal)
Be*	0.1	- 10	1 - 5	10
B	2	- 100	5 - 30	100
F	10	- 500	50 - 250	500
Cr	1	- 100	10 - 50	100
Ni	1	- 100	10 - 50	100
Co	1	- 50	1 - 10	50
Cu	2	- 100	5 - 20	100
Zn	10	- 300	10 - 50	300
As	1	- 50	2 - 20	50
Se	0.1	- 10	1 - 5	10
Mo	0.2	- 10	1 - 5	10
Cd*	0.01	- 1	0.1 - 1	5
Hg*	0.01	- 1	0.1 - 1	5
Pb	0.1	- 10	0.1 - 5	100

*   special reservation

5.2.9 Health Consideration

Sewage and sewage sludge, and also compost from solid waste treated with sludge, are usually regarded as potentially hazardous to human health or living organisms if the treatment was insufficient. According to Figure 53, there are many treatment steps available for sludge, but only two alternatives for the final removal - dumping or spreading on farmland. While many treatment steps still result in a hazardous product, special considerations are necessary for admissible and inadmissible sludge application to cropland, Figure 58. Sanitary regulations give information on the application of different kinds of sludges, i.e. to cropland or grassland, in vineyards or orchards, in nurseries or gardens, in the growth period or in winter. Composts from solid waste mixed with sewage sludge are unobjectionable, if the composting operations are well managed. The major factors in the destruction of pathogenic organisms in composting are heat and antibiotic reactions (Golueke, 1973).

		Reserve crop	Crop land		Grass land Forage crop		Vineyard	Orchard no filler	Nursery	Garden vegetable land
			No GS	GS	No GS	GS	No GS	No GS		
Raw sludge	h	+	-	-	-	-	-	-	-	-
Sludge from premises, treatment plants and earth basins	h	+	+	-	-	-	-	-	+	-
Liquid drained / natural dried } anaerobically or aerobically stabilized sludge	h h h	+	+	-	+	-	+	+	+	-
Chemically } conditioned by heat } sludge	h									
Artificially dried sludge pasteurized sludge (raw, stabilized, chem. cond.) composted sludge		+	+		+		+	+	+	+

h = hazardous   + admissible   - inadmissible   GS growth season

Fig. 58   Admissible and inadmissible sludge application to cropland

The effectiveness of land treatment in removing contaminants from wastewater is high. Data indicate nearly complete removal of BOD, pathogenic bacteria, viruses and phosphorus, while the level of removal of nitrogen, sulphates and chlorinated hydrocarbon pesticides is high. Land treatment offers a safer means of treating wastewater than any other general method now available (Stevens, 1972).

Public health standards for human use of products of biologically based waste recycling systems should be adjusted to the level of animal and human contact involved. Standards for such uses should take into consideration the

special chemical and micro-biological problems associated with urban and industrial wastes. However, such standards should take into account the fact that it is unreasonable to expect to achieve absolutely zero risk levels in any one area of environmental exposure.

Epidemiological surveillance must be maintained not only to define the rates of exposure but also to establish the ecology of viruses, pathogens and parasites so that decontamination schemes can be identified. Urban wastes contain higher amounts of polycyclic aromatic hydrocarbon (PAH) than soils, Table 25. The application of urban waste composts at a rate of 100 t/ha has increased the concentration of PAH in soils remarkably (Ellwardt, 1976). However, the investigations did not indicate significant differences in the amounts of PAH in the plants originating from soils whether treated or not with waste compost. The concentrations of some PAH in sewage sludge, solid waste compost, soils and plant materials are summarized in Table 26 (Ellwardt, 1976)

Table 26   AMOUNTS OF POLYCYCLIC AROMATIC HYDROCARBONS IN SEWAGE SLUDGE, WASTE COMPOST, SOIL AND PLANT MATERIALS
(in ppb or μg/kg)

	Sludge (98% water)	Compost	Soils un-treated	Soils treated	Potatoes (tubers)	Potatoes (haulms)	Oats (grain)	Oats (straw)
Benzo (b, k, j) fluorathene	2 962	3 400	112.0	160.0	5.4	42.4	21.2	31.5
Benzo (e) pyrene	1 247	1 750	48.3	83.0	2.6	24.8	7.5	5.3
Benzo (a) pyrene	806	680	23.2	40.0	0.8	7.9	1.5	8.2
Perylene	250	131	4.2	7.1	6.2	5.0	13.1	5.6
Indeno (1, 2, 3-cd) pyrene	281	457	17.5	29.0	1.7	1.0	5.4	1.0
Dibenz (a, h) anthracene	684	785	38.1	60.5	5.0	10.0	20.2	1.0
Dibenz (a, c) anthracene	257	134	13.4	26.0	-	8.8	1.0	13.3
Benzo (ghi)perylene	610	802	32.1	59.9	5.0	11.8	26.6	17.7

The health hazards, especially the carcinogenic risks, are a cause for concern. The actual health hazard to human beings and animals from long term exposure to concentrations of less than one ppm of possible carcinogenic compounds is extremely difficult, perhaps impossible, to evaluate because of insufficient data. Until bioassay techniques are refined enough to evaluate the chronic effects of extremely low levels of these compounds, their concentrations can only be monitored to establish a cause and effect relationship, if there is one.

Waste reuse standards should provide levels of protection commensurate with other comparable risks that society finds acceptable. Biologically based waste recycling systems should be designed so as to optimize production of economically and socially useful products, final waste disposal and/or water quality improvement. Major benefits from such systems may include savings in costs of fertilization, cultivation and irrigation of crops (D'Itri, 1976).

6.   ECONOMICS OF USING ORGANIC MATERIALS AS FERTILIZERS

It has been reported that immediate economic gains from using organic materials as fertilizers do not compare very favourably with inorganic fertilizers; however, it is significant that if long term benefits, such as slow release of plant nutrients, especially nitrogen, improvement of physical and biochemical conditions of soils, checking of soil erosion, increasing the efficiency of utilization of chemical fertilizer, sustaining the yields of high yielding varieties, and reducing air and water pollution (thus improving the environment), are taken into consideration, the application of organic materials as fertilizers will produce good economic results. Furthermore, in the light of the recent considerable increase in the price of inorganic fertilizers and the scarcity of foreign exchange in most developing countries, the large scale use of organic materials as fertilizers is a sound economic proposition.

6.1   THE ECONOMICS OF USING ORGANIC MATERIALS AS FERTILIZERS

Even in mechanized and intensive agriculture in the developed countries, nitrogen is obtained from diverse sources for plant nutrition. Bucher et al. (1974) reported that in agriculture in mid-Europe 150 kg N/ha comes from the following sources:

83	kg	N from mineral fertilizers
40	kg	N from organic manures
1.5	kg	N content of seed
5	kg	N fixation by symbiosis
10	kg	N fixation by asymbiosis
10	kg	N in precipitation
Average = 149.5	kg	N/ha agricultural land

About 55% of the nitrogen added to fields is in the form of mineral fertilizers. A small portion of the inorganic nitrogen compounds is contained in precipitation as rain or snow. So in total about 60% of the nitrogen is added in the form of inorganic nitrogenous ions and about 40% comes into the soil as organic nitrogenous materials.

Through investigstions with the isotope ^{15}N, it was demonstrated that, on average, about 50% of the nitrogen content of the harvested plant originates from mineral fertilizers and the rest from the organic constituents of the soil by mineralization through microbial activity. In many soils in developing countries in the warmer regions, the humus content is relatively low due to climatic conditions and therefore the reservoir of nitrogen in the soil is small.

Thus the foremost significance of organic fertilizer and soil organic matter in the economy of agriculture is the slow availability of nitrogen from them which is in tune with the requirements of plant growth. Therefore, organic fertilizers are of great value for the agriculture of the developed as well as developing countries.

In addition to nitrogen, organic materials and soil organic matter provide other plant nutrients such as P, K, Ca, Mg and trace elements. Furthermore, soil organic matter provides the energy source for the growth of the microbial population which is responsible for a number of significant biochemical processes. Soil organic matter also provides plant nutrients from sources other than itself (e.g. release of P or K from soil inorganic materials). The availability of

phosphorus is increased by the addition of organic materials, partly by a possible increase of microbial activity. It has also been reported by some workers that free organic compounds and the decomposition products of humus have a beneficial influence on plant growth. Some workers have produced evidence that the decomposition products of soil organic matter check the incidence of plant diseases. Although the economic gains from these benefits of soil organic matter are considerable, it is difficult to state them clearly in economic terms.

In addition, organic matter checks soil erosion and helps soil conservation. It has been reported that there is an inverse relationship between the organic matter content of soils and soil erosion and water run-off. Soil erosion is a serious problem in tropical and subtropical climatic conditions, therefore, the use of organic materials as fertilizers, from the point of view of helping to solve this problem, is of some economic significance.

It must be emphasized that the large scale use of organic materials as fertilizers depends on a number of factors such as climatic conditions, level of agricultural mechanization, availability of low cost organic materials in large quantities, specific needs of soils to ameliorate their physical conditions, influence of constraints such as water supply and transport charges and the substantial economic gain to the farmer by using them. Therefore, the economics of using organic materials as fertilizers depends on the local conditions prevalent in any country.

Organic materials, especially cow dung, apart from its manurial value, can also provide biogas which can be used for cooking, running irrigation pumps and rural electrification. Table 27 shows the amount of manure and gas obtained from one ton of fresh dung according to Garg et al. (1971).

Table 27   MANURE AND GAS PRODUCED BY ONE TON OF FRESH DUNG

	1 000 kg (0.25% nitrogen)	
	Traditional method	Through gas plant
a) Organic matter loss by decomposition	500 kg	270 kg
b) Nitrogen loss by decomposition	1.25 kg	nil
c) Final manure quantity	500 kg	730 kg
Quality Nitrogen % on dry basis	1.0 %	1.37 %
d) Additional advantage	-	2 000 ft^3 gas for cooking

These figures illustrate that the simultaneous production of manure and gas from cattle dung and organic wastes is an attractive proposition economically.

From the economic point of view one should differentiate between rural and urban residual products when using organic materials as fertilizers. The main rural waste products are plant residues and excreta from animals and human beings. After harvest the residues from crops often remain on the fields and can be ploughed in with no transport cost, but in most cases additional nitrogen fertilization is necessary so that the lack of nitrogen fixation by microbial activity during the rotting processes does not influence plant growth negatively.

Some plant residues, e.g. cereal straw, are used in stables as litter and later, when mixed with animal excreta, become manure from which carbon dioxide is released by fermentation. The amount of carbon in the initial material decreases and the nitrogen content increases in the fermented products. Normal stable manure has a nitrogen content of about 3% in the dry matter and the C/N-ratio is between 10 and 20; the water content is between 50 and 70%. Under normal conditions, it is more economic to transport this nitrogen-enriched material with its better C/N-ratio from the village to the fields than to transport plant residues, like straw, back from the village, for instance after threshing, because the nitrogen content of straw is only about 0.3% in the dry matter and the C/N-ratio 80 - 100. Threshing should be as near as possible to the fields when straw is not used for stable manure. When straw or other plant residues and dried dung are needed for fuel, a programme for the cultivation of fast growing bushes and trees should be organized, for instance as proposed by Swaminathan (1974).

Human and animal excreta is relatively rich in plant nutrients (see Chapter 5) and has a value that justifies its transport to the fields (taking the necessary hygienic precautions). These materials can be used profitably in horticulture, generally after composting with plant residues.

In towns it cannot be avoided that residues from human sources are mixed with industrial wastes to some extent and this causes additional problems when used for plant production. It must be emphasized that these wastes contain pollutants such as heavy metals or organic compounds e.g. detergents, poly-chlorinated compounds, polycyclic aromatic hydrocarbons and others, some of the last mentioned being carcinogenic compounds. Controls must be carried out to see if the products of upgraded rural wastes are usable for plant production or not, and perhaps processes must be inserted to decrease concentrations of harmful constituents.

Around larger towns there is usually an industrial area precluding the possibility for deposition of upgraded town wastes and for this reason additional costs are incurred transporting it to more distant locations where the upgraded products can be used. They have a nitrogen content between 0.2 and 0.5% and a high C/N-ratio of about 50. These data demonstrate that such products can have more of an effect as soil conditioners than as sources of plant nutrition. The farmer is only interested in the benefits of these products for his plant production, the inhabitant of the town in a regulated waste disposal. Therefore it seems justified that the costs be shared between both; but the percentage of distribution of the costs depends on the local conditions in each case and on the interest of the parties.

In some cases it is possible that the costs of upgrading urban waste products could be diminished by using the biogas (mainly methane) for power or cooking. The gas is formed during anaerobic fermentation of the organic compounds in the waste waters. The value of the residual organic matter after fermentation is almost the same for agricultural purposes as the initial material. Furthermore, the composition of inorganic ions in the liquid phase is not changed during this process. This is important when using the acqueous phase for irrigation or sprinkling.

The amount of organic material required for nitrogen fertilization at a rate of 100 kg/ha is about 20 000 kg, while for mineral fertilizers it is 450 - 650 kg of materials, from which it can be deduced that the expenditure for moving organic materials for use as fertilizers is usually higher than that for mineral fertilizers. It depends on the social, economic and distribution systems.

The utilization of organic wastes as fertilizers is of great economic significance from the public hygiene, pollution control and environmental

protection points of view. In the developed as well as in the developing countries organic waste is usually disposed of in the following ways:

i.   it is dumped on nearby land where it is likely to encourage fly breeding;

ii.   it is disposed of (treated or untreated) in nearby rivers or the sea where it adversely affects aquatic life;

iii.   it is destroyed by incineration, but this process pollutes the atmosphere and destroys the manurial value of wastes.

Therefore, from those points of view it is highly desirable that organic wastes be used as a source of manure and gas so that maximum economic benefits may be obtained from them.

When determining the true economic value of using organic materials as fertilizers it is absolutely essential to take into consideration short as well as long term benefits to agricultural production, to the economic value of gas production and any resultant benefit to public health, pollution control and environmental protection.

6.2 POTENTIAL AND ECONOMIC IMPLICATIONS OF USING ORGANIC MATERIALS AS FERTILIZERS IN THE DEVELOPING COUNTRIES

Recently van Voorhoeve of the World Bank (1974) worked out the potential for using organic materials as fertilizers in the developing countries(in Table 28) and in Table 29 he gives the value of organic nutrients compared to chemical fertilizers based on 1973 f.o.b. world prices.

These tables present only a rough estimate of the potential of using organic materials for soil productivity in the developing countries and the economic implications, as little reliable research work has been carried out in this field. Furthermore, owing to political, social, technical and economic reasons, it is generally not possible for the developing countries to utilize this potential fully; at best they may use only 60 - 80% of the potential in exceptional circumstances. Moreover, while obtaining N from animal manure, night soil, sewage, etc. for plant nutrition, there may be losses from 0 - 50% of the total nitrogen present in these manures.

Despite these facts, the study by van Voorhoeve clearly presents an extraordinary potential for the use of organic materials as fertilizers in the developing countries with attractive economic implications. Even if only 10 - 20% of this potential is exploited for soil productivity, organic materials can contribute very significantly to solving the present day food crisis.

Van Voorhoeve further reported in the same paper that in 1971, the total theoretical production of plant nutrients from organic materials could be 7.8 times greater than the actual consumption of mineral fertilizers in that year (13.2 million metric tons). Significantly, Table 29 indicates that in economic terms, the total value of this theoretical production of plant nutrients from the organic materials in 1971 could be over 16 thousand million US dollars. Van Voorhoeve has also estimated that in 1980/81 the consumption of mineral fertilizers (N and P) in all the developing countries is likely to be about 30 million tons. On the other hand, he reported that in 1980/81 the likely theoretical production of these plant nutrients from organic materials in the developing countries could be at least 80.4 million metric tons. These impressive statistics present a very strong case for efforts to obtain plant nutrients from organic materials for soil productivity in the developing countries with the technical assistance of International Agencies.

Table 28   TOTAL ANNUAL PRODUCTION OF SOIL NUTRIENTS
                    (N, P, K) THROUGH ORGANIC WASTES IN THE
                    DEVELOPING WORLD
                    1971 (actual) and 1980 (estimated) [1]

Source		N	P	K
		(million metric tons of nutrients)		
Human:	1971	12.25	2.87	2.61
	1980	15.26	3.57	3.25
Cattle:	1971	17.80	4.91	14.12
	1980	22.25	6.14	17.65
Farm Compost:	1971	9.54	3.34	9.54
	1980	11.93	4.18	11.93
Urban Compost:	1971	.48	.38	.57
	1980	.60	.48	.71
Urban Sewage:	1971	1.43	.29	.86
	1980	1.79	.36	1.08
Other [2]	1971	6.63	4.44	11.35
	1980	8.29	5.55	14.19
TOTAL:	1971	48.13	16.23	39.05
	1980	60.12	20.28	48.81

[1]   Excludes Central America and Oceania, includes Socialist Asia.

[2]   Bone-meal, poultry litter, bagasse, sheep/goat litter, oil cake, press-
       mud. (Several other sources were not included due to small potential
       for all developing world.)

Table 29   VALUE OF N, P AND K FOUND IN WASTES OF THE
                    DEVELOPING WORLD AS COMPARED TO CHEMICAL
                    FERTILIZERS
                    (at 1973 world f.o.b. prices in millions of $US) [1]

		N	P	K	Total
Organic	1971	9 626	4 058	2 499	16 183
	1980	12 024	5 070	3 124	20 218
Chemical	1971	7 000	5 597	1 246	13 843
	1980	11 380	7 775	1 638	20 793

[1]   The individual farmer pays local prices, which are higher than world
       prices because of transport, storage and commercial costs; he may be
       able to benefit from government subsidies on fertilizer prices. In
       Table 28, the value of N is based on the world f.o.b. price of urea
       (45% N) at US$ 70-105/t, which means a price of $ 155-233/t of pure N;
       the average value was set at a median of US$ 200/t. P-value is based
       on triple superphosphate (21% P) at $ 120/t, which means $ 250/t of P.
       The K-value is based on potassium chloride (62% K) at $ 40/t, which
       means $ 64/t of K.

6.3 SUGGESTIONS FOR FURTHER RESEARCH ON THE ECONOMICS OF APPLYING ORGANIC MATERIALS AS FERTILIZERS

Unfortunately, little research work has been done on the economics of using organic materials as fertilizers especially in the developing countries. Research in this field should include:

i. comprehensive studies to establish the true economic values of organic fertilizers, especially in the developing countries, in order to determine the cost/benefit analysis, including benefits for soil productivity (short and long term), environment and public health;

ii. cost/benefit analysis of the various procedures of collecting, processing and distributing organic fertilizers (prepared from the low cost materials available in sufficient quantities in the country);

iii. at the farm level, studies on the economics of using mineral fertilizers in combination with various dosages of organic materials such as crop residues, compost, bones, animal manure and peat, night soil and sludge, etc.

iv. studies on the economics of the various constraints to the large scale application of organic materials as fertilizers, such as low availability of water, high transport charges, etc. Subsequently, research work should be carried out to solve these problems so that the application of organic fertilizers to increase soil productivity will produce significant economic benefits.

7. RECOMMENDATIONS AND CONCLUSIONS

7.1 GUIDELINES

In view of the current world food crisis, the considerable increase in the price of mineral fertilizers, and the comments offered in this bulletin on the present situation regarding the use of organic materials as fertilizers, the developing countries should seriously reconsider their agricultural research, education and extension programmes with the idea of including plans to utilize organic materials as fertilizers on a large scale. In the formulation of these plans, it is suggested that they and international organizations follow these guidelines:

i.   there should be maximum agricultural production with the least possible utilization of costly energy;

ii. organic materials should be used in large quantities as fertilizers thus reducing the consumption of mineral fertilizers (consequently the consumption of energy will be reduced). Furthermore, the efficiency of the mineral fertilizers used would be increased;

iii. steps should be taken to organize short as well as long term research on soil organic matter and organic manures;

iv. short term research likely to produce fruitful results within 3-4 years should be initiated immediately by national governments with external assistance if necessary; on the other hand, long term research could be carried out by national governments with the assistance of international agencies, research foundations and the developed countries;

v.   in order to create a cadre of people with the right background for research, education and extension work on soil organic matter, there should be suitable changes in agricultural education at all levels;

vi. efforts should be made to develop and intensify extension work with a view to propagating large scale use of organic materials as fertilizers;

vii. while organizing activities on the large scale use of organic materials as fertilizers, special emphasis should be placed on the development of root nodule bacteria (Rhizobium), legumes, animal manures, composting and recycling of city and rural wastes;

viii. studies should be carried out on safe and economic methods of large scale collection, processing, distribution and utilization of organic wastes. The possible adverse effects of toxic constituents of wastes such as heavy metals or organic compounds like residual products of pesticides, or polycyclic aromatic compounds should be studied and suitable solutions found for these problems;

ix. studies should be carried out on the social and economic implications of the large scale use of organic manures as fertilizers;

x.   activities should be organized to popularize, as much as possible, the use of biogas and the necessary social infrastructure for this should be established;

xi.   the utility of organic wastes from the standpoint of public health, pollution control, and environment protection should be assessed;

xii.   in order to co-ordinate, evaluate critically and promote research, extension and educational activities in this field, there should be regular discussions on this subject; such meetings of experts should not only examine critically all the work in progress in this field under the auspices of FAO projects and at international institutes [1] but should also make recommendations for further work in this field;

xiii.   it must be realized that the world is an inter-dependent socio-economic and ecological system; therefore, international co-operation is absolutely necessary to promote the large scale use of organic materials as fertilizers for food production, especially in the developing countries.

7.2   RESEARCH

During the FAO consultation in 1974 on organic materials as fertilizers, recommendations were made for research work on this subject. The recommendations included proposals for short and long term research and are described in FAO Soils Bulletin No. 27, Organic Materials as Fertilizers, section G. pp. 379-382.

7.3   EXTENSION

Suggested steps to propagate the use of organic materials as fertilizers in different parts of the world are given in FAO Soils Bulletin No. 27, section G, pp. 382-383.

7.4   EDUCATION

Suggestions for radical changes in education for research workers in the field of fertilization by organic material are listed in FAO Soils Bulletin No. 27, section G, pp. 383-384.

7.5   PUBLICATIONS

Proposals have been made (FAO Soils Bulletin No. 27, section G, pp. 384-5) for improving the preparation and distribution of publications dealing with the subject of organic materials as fertilizers.

7.6   INTERNATIONAL CO-OPERATION

It is essential for international scientific communities working in the field of soil organic matter and organic manures to co-operate in promoting the large scale use of organic fertilizers. Suggestions for achieving such co-operation are given in section G, p. 383, of FAO Soils Bulletin No. 27.

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[1]   International Rice Research Institute (IRRI) in the Philippines; the International Crop Research Institute for the Semi-Arid Tropics (ICRISAT), India; the International Institute of Tropical Agriculture (IITA), Nigeria; Centro Internacional de Majoramiento di Maiz y Trigo (CIMMYT), Mexico; and the Centro Internacional de Patatas (CIP), Colombia, etc.

On the basis of the brief account of the contribution of soil organic matter to soil productivity presented in this Bulletin, it can be reasonably concluded that organic materials must be utilized to improve plant nutrition, to develop soils in order to increase their productive capacity and to contribute to the solution of the present day world food crisis. In view of the shortage and high price of mineral fertilizers, it is desirable that the developing countries make use of organic materials to lessen the deficiency of plant nutrients by the addition of agricultural residual products such as the residues of plants, and animal manures. Where the possibility exists, town and certain industrial wastes should also be used. Apart from providing nutrients, an improvement in the physical and mechanical conditions of the soil for plant growth results from these treatments. Furthermore, there is an increase in the efficiency of utilization of the added inorganic fertilizers and the economic value of the mineral fertilizers, especially of nitrogen, is thus raised. The more dense the population in a region, the more the utilization of residual organic materials contributes to pollution control and environment protection. In view of the manifold advantages of organic fertilizers and their availability in large amounts in most of the developing countries, the economics of their use is sound.

Soil was, and will be, the main tool for production of food by the plants that grow on it, even though the production of foodstuffs such as proteins by single cell cultures, etc. is possible. The technical equipment for such biotechniques requires capital, generally rather a lot, and can only be justified in special cases. But the main producer of food is still the farmer in the field who must use the techniques available to him and that he can afford with his relatively small financial means.

The interdependence of the various factors is summarized in Figure 59. Food grown on fields is transported from them for the nutrition of men and animals. The fertility of the soil must be regenerated by the addition of nutrients in the form of fertilizers produced in factories. The raw materials for the production of fertilizers come from mines or, in the case of nitrogen, from the air.
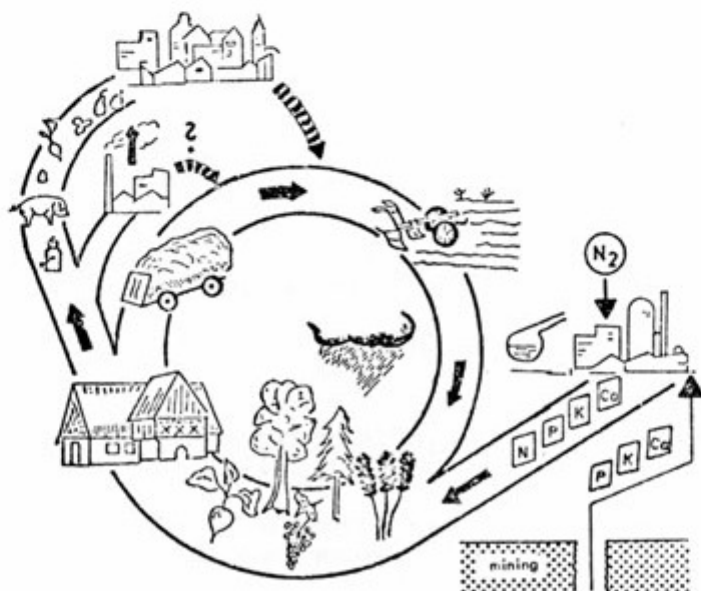
Fig. 59   Cycle of nutrients-fertilization-plant and animal
              production-recycling of residual organic materials

Recycling agricultural residues by using them on the fields does not deal with problems such as municipal wastes, because most of the materials are derived from plants or excreta and the composition of the inorganic part is comparable to that of the growing plants in the next vegetation period. The decomposition of straw or other plant material and of animal manures depends on environmental conditions. It might be worth trying to channel these conditions towards causing an increase in plant production.

The use of municipal wastes can often cause problems, because various heavy metals and some organic compounds are present in the products finally offered to the farmers. The extent of the compatability of these admixtures and their behaviour in the Plant - Soil system is not yet completely known and needs further investigations. In many cases organic residues from industry contain noxious constituents, therefore their use in agriculture is limited.

However, in order to use organic materials as fertilizers on a large scale, "political will" on the part of the developing countries is absolutely essential. They need to intensify their present activities in this field and prepare plans for the wide use of organic materials as fertilizers in which case the guidelines given in this Bulletin will be useful. Furthermore, to use these materials extensively as fertilizers it is essential not only to organize short and long term research in the developed countries, but also to utilize the results of this research in conjunction with appropriate administrative measures. A number of significant problems are suggested for research and their solution should go a long way to promote the use of organic materials as fertilizers. In addition, countries should develop and reorganize their agricultural education at all levels and their extension services to propagate the use of organic materials as fertilizers and to create the right type of man power in this field. A number of recommendations for this purpose have been incorporated in the Bulletin.

Finally, as the world is an interdependent socio-economic and ecological system, co-operation between the developing countries and the international agencies, co-operation among the developing countries of the same region, and co-operation between the developing countries and the developed countries is essential to propagate the use of organic materials as fertilizers in order to increase food production.

REFERENCES

Allison F.E. and Sterling L.D. Nitrate formation from organic matter in relation to total
1949   nitrogen and cropping practices. Soil Sci. 67:239-252.

Allison F.E. Soil organic matter and its role in crop production. Elsevier, Amsterdam,
1973   London, New York.

Anderson G. Other organic phosphorus compounds. In: Soil Components 1, Organic
1975a   Components. J.E. Gieseking (Ed), Springer-Verlag, New York, Heidelberg,
         Berlin. p. 305-331.

Anderson G. Sulfur in soil organic substances. In: Soil Components 1, Organic
1975b   Components. J.E. Gieseking (Ed), Springer-Verlag, New York, Heidelberg,
         Berlin. p. 333-341.

Anderson J.P.E. and Domsch K.H. Participation of bacterial and fungal populations in
1975   mineralization of selected organic substances in soil. Trans. Int. Symp. Humus
         et Planta VI, Prague, 18-22 August 1975. p. 211-214.

Appelt H., Coleman N.T. and Pratt P.F. Interactions between organic compounds,
1975   minerals and ions in volcanic-ash-derived soils. II. Effects of organic com-
         pounds on the adsorption of phosphate. Soil Sci. Soc. Amer. Proc. 39:628-630.

Baden W. The types of peat deposits used in present-day agriculture and the methods of
1972   their utilization. Proc. 4th Int. Peat Congr. 3:7-20. Otaniemi, Finland.

Balandreau, Rinaudo J.G., Fares-Hamad J. and Dommergues Y. N-fixation in paddy soils.
1975   In: Nitrogen fixation by free-living microorganisms. (In press)

Banse H.J. Beeinflussung der physikalischen Bodeneigenschaften durch Kompostgaben.
1961   IAM Informationsblatt 13:30-35, Zürich.

Bartholomew W.V. Mineralization and immobilization of nitrogen in the decomposition of
1965   plant and animal residues. In: Agron. Monograph 10: Soil nitrogen p. 285-306.
         Amer. Soc. Agron., Madison, Wisconsin.

Bartholomew W.V. and Kirkham D. Mathematical descriptions and interpretations of
1960   culture induced soil nitrogen changes. Trans. 7th Int. Congr. Soil Sci. 2:471-477.

Bartlett J.B. The effect of decomposition of the lignin of plant materials. Iowa State Coll.
1939   J. Sci. 14:11-13.

Bartlett J.B. and Norman A.G. Changes in the lignin of some plant material as a result of
1938   decomposition. Soil Sci. Soc. Amer. Proc. 3:210-216.

Bartlett J.B., Smith F.P. and Brown P.E. Lignin decomposition in soils. Proc. Iowa
1937   Acad. Sci. 44:97-101.

Bate-Schmith E.C. and Lerner N.H. Systematic distribution of leuco-anthocyanins in
1954   leaves. Biochemie J. 58:126-132.

Bath, Schierenbeck, Rudolph and Ruwenstroth. Gutachten zur Abwasserverregnung
1976   Braunschweig, Gesellschaft für Landeskultur Bremen.

Behrenberg V. and Gobler. Versuche über Manganmangel an verschiedenen Kultur-
1943   pflanzen. Diss. Univ. Bonn.

Belav L.   Chemische Untersuchungen heimischer Torfbildner zur Kenntnis der Umwandlung
1967   von Pflanzenstoffen unter natürlichen und künstlichen Bedingungen.   Dissertation
          Rostock.

Berlin J., Barz K., Harms H. and Haider K.   Degradation of phenolic compounds in plant
1971   cell cultures.   Febs Letters 16:141-146.

Betremieux R.   Etude expérimentale de l'évolution du fer et du manganése dans les sols.
1951   Ann. Agron. 2:193-295.

Beutelspacher H.   Elektronenmikroskopische Untersuchungen über den Ton-Humus-Komplex.
1955a   Proc. Nat. Acad. Sci. (India) Allahabad 24, Sect. A, Part II.

Beutelspacher H.   Wechselwirkung zwischen anorganischen und organischen Kolloiden des
1955b   Boden.   Z. Pflanzenernähr., Düng., Bodenk. 69:108-115.

Bloomfield C.   Experiments on the mechanism of gley formation.   J. Soil Sci. 2:169-211.
1951

Blumer M.   Benzopyrenes in soil.   Science 134:474.
1961

Boguslawski E.v. and Saalbach.   Die Wirkung von Thymochinon auf das Wachstum von
1960   Sommergerste in Abhöngigkeit von der Höhe der Stickstoffdüngung.   Z. Acker- u.
          Pflanzenbau 110 (2):153-162.

Bondietti E., Martin J.P. and Haider K.   Stabilization of amino sugar units in humic-type
1972   polymers.   Soil Sci. Soc. Amer. Proc. 36:597-602.

Bondietti E., Martin J.P. and Haider K.   Influence of nitrogen source and clay on growth
1971   and phenolic polymer production by Stachybotrys species, Hendersonula
          toruloidea and Aspergillus sydowi.   Soil Sci. Soc. Amer. Proc. 35 (6):917-922.

Bosse I.   Ein Versuch zur Bekämpfung der Bodenerosion in Hanglagen des Weinbaues durch
1968   Müllkompost.   Weinberg und Keller 15:385-397.

Bould C.   Chelated iron compounds for the correction of lime-induced chlorosis in fruit.
1955   Nature 175:90-91. London.

Boyle J.R., Voigt G.K. and Sawhney B.L.   Chemical weathering of biotite by organic
1974   acids.   Soil Sci. 117:41-45.

Bradley D.B. and Sieling D.H.   Effect of organic anions and sugars on phosphate precipita-
1953   tion by iron and aluminium as influenced by pH.   Soil Sci. 76:175-179.

Braids O.C. and Miller R.H.   Fats, waxes and resins in soil.   In: Soil Components 1,
1975   Organic Components.   J.E. Gieseking (Ed), Springer-Verlag, New York, Heidel-
          berg, Berlin.   p. 343-368.

Bremner J.M.   Organic nitrogen in soils.   In: Agron. Monograph 10: Soil nitrogen p. 93-149.
1965a   Amer. Soc. Agron., Madison, Wisconsin.

Bremner J.M.   Organic forms of nitrogen.   Ch. 85 Methods of Soil Analysis.   Agron. Mono-
1965b   graph 9.   Amer. Soc. Agron., Madison, Wisconsin.

Bremner J.M.   The nitrogenous constituents of soil organic matter and their role in soil
1968   fertility.   Pontificiae Acad. Scient. Scripta Varia 32:143-185.

Bremner J.M. and Hauck R.D.   Perspectives in soil and fertilizer nitrogen research: Abstr.
1974   Int. Soil Sci. Soc. Vol. IX, 13-29.

Brink H. Work on terminology in Sweden. Conference at the International Trade Fair on
1973 Waste Handling. Avall 73, Jönköping, Sweden. 27-31 August 1973.

Broadbent F.E. Modification in chemical properties of straw during decomposition. Soil
1954 S ci. Soc. Amer. Proc. 18:165-169.

Broadbent F.E. Turnover of nitrogen in soil organic matter. Pontificiae Acad. Scient.
1968 Scripta Varia 32:61-84.

Bruckert S., Jaquin F. and Metche M. Contribution à l'étude des acids phénols présents
1967 dans les sols. Bull. d'Ecole Nationale Supérieure Agronomique de Nancy IX (II):
73-92.

Buchner A. and Sturm H. Theoretische N-Bilanz bei ausgewählten Kulturen, Fruchtfolgen
1974 und Gebieten. Landwirtsch. Forsch. Sonderh. 30 (II):78-92.

Bundy L.G. and Bremner J.M. Effects of substituted p-benzoquinones on urease activity
1973 in soils. Soil Biol. Biochem. 5:847-853.

Bundy L.G. and Bremner J.M. Effects of urease inhibitors on nitrification in soils. Soil
1974 Biol. Biochem. 6:27-30.

Burge W.D. and Broadbent F.E. Fixation of ammonia by organic soils. Proc. Soil Sci.
1961 S oc. Amer. 25:199-204.

Burges N.A., Hurst H.M. and Walkden S.B. Nature of humic acid. Nature 199:696.
1963

Burges N.A., Hurst H.M. and Walkden S.B. The phenolic constituents of humic acids and
1964 their relation to the lignin of the plant cover. Geochim. Cosmochim. Acta 28:
1547-1554.

Butler P.C. and Bray R.H. Effect of the zinc chelate of ethylenediaminetretraacetic acid
1956 on plant uptake of zinc and other heavy metals. Soil Sci. Soc. Amer. Proc. 20:
348-351.

Ceshire M.V., Cranwell P.A., Falshaw C.P., Floyd A.J. and Haworth R.D. Humic
1967 Acid-2. Tetrahedron, 23:1669-1682.

Chaminade M. Action des constituants de la matière organique des sols sur le metabolisme
1965 des plants, la croissance et le rendement. C.R. hebd. Séance Acad. Agric.
France 17:1139-1145.

Chaminade R. Effet physiologique des constituants de la matière organique des sols, sur
1966 le metabolisms des plantes, la croissance et le rendement. In: The Use of Iso-
topes in Soil Organic Matter Studies. Report of the FAO/IAEA Tech. Meeting.
Pergamon, Oxford. pp. 35-47.

Chaminade R. Rôle spécifique de la matière organique sur la nutrition et le rendement des
1968 végétaux. Pontificiae Acad. Scient. Scripta Varia 32:777-800.

Charreau C. Organic matter and biochemical properties of soil in the dry tropical zone of
1975 West Africa. In: Soils Bulletin 27, FAO Rome, pp. 313-335.

Child J.J. Nitrogen fixation by Rhizobium sp. in association with non-leguminous plant cell
1975 cultures. Nature 253:350-351.

Christensen P.D., Toth S.H. and Bear F.E. The status of soil manganese as influenced
1951 by moisture, organic matter and pH. Soil Sic. Soc. Amer. Proc. 15:279-282.

Christeva L.A., Fot L.V., Gorovaia A.I. and Aizikovich L.E. The influence of physio-
1972   logically active acids upon the utilization of heightened nitrogen doses, the
            nucleic and albuminous metabolism. Proc. 4th Int. Peat Congress 4:7-18.
            Otaniemi, Finland.

Colonna R.A. Decision-makers guide in solid waste management. U.S. Environmental
1976   Protection Agency, Washington D.C.

Cotter D.J. and Mishra U.N. The role of organic matters in soil manganese equilibrium.
1968   Plant and Soil 29:439-448.

Coulson C.B., Davies R.I. and Lewis D.A. Polyphenols in plant, humus and soil: 1. J.
1960   Soil Sci. 11:20-29.

Dalton J.A., Russell G.C. and Sieling D.H. Effect of organic matter on phosphate avail-
1952   ability. Soil Sic. 73:173-181.

Dhar N.R. The value of organic matter, phosphates and sunlight in nitrogen fixation and
1968   fertility improvement in world soils. Pontificiae Acad. Scient. Scripta Varia
            32:243-360.

Dhar N. World food crisis and land fertility improvement. Kamala Lectures for 1953,
1972   University of Calcutta, India. 247 p.

Dilworth M.J. Acetylene reduction by nitrogen-fixing preparations from Clostridium
1966   pasteurianum. Biochim. biophys. Acta 127:285-294.

D'Itri F. Wastewater renovation and reuse: An urgent environmental need. Conference
1975   at the Rockefeller Foundation Center in Bellagio, Italy. 16-21 July 1975.

Döbereiner Johanna. Non-symbiotic nitrogen fixation in tropical soils. Pesquisa Agro-
1968   pecuaria Bras. 3:1-6.

Döbereiner Johanna and Day J.M. Associative symbioses in tropical grasses: characteriza-
1974a   tion of microorganisms and dinitrogen fixing sites. Intern. Symposium on N_2-
            fixation - Interdisciplinary Discussions, Washington State Univ.

Döbereiner Johanna and Day J.M. Associacao de bacterias fixadores de nitrogenio com
1974b   raizes de gramineas. Reuniao Latinoamericana do Trigo, Porto Alegre.

Dolar S.G., Keeney D.R. and Walsh L.M. Availability of Cu, Zn and Mn in soils. III.
1971   Predictability of plant uptake. J. Sci. Food Agric. 22:282-286.

Dormaar J.D. Humic acid associated phosphorus in some soils of Alberta. Can. J. Soil
1963   Sci. 43:235-241.

Duncan A. Economic aspects of the use of organic materials as fertilizers. In: Soils
1975   Bulletin 27, FAO Rome, pp. 353-378.

Durand G. Les enzymes dans le sol. Revue d'Ecologie et de Biologie du Sol 2:141-205.
1965

El-Bassam N., Tietjen C. and Mertens F. Nitrat-, Nitrit und Ammoniak-N im Boden und
1974   Bodenwasser sowie Aufnahme durch Markstammkohl und Zuckerrüben bei Zufuhr
            hoher Klärschlammgaben. Landwirtsch. Forsch. 30 (II):29-38.

El-Bassam N., Poelstra P. and Frissel M.J. Chrom und Quecksilber in einem seit 80
1975   Jahren mit städtischem Abwasser berieselten Boden. Zeitschr. Pflanzenernähr.,
            Bodenkunde 138:309-316.

Egawa T. The use of organic fertilizers in Japan. In: Soils Bulletin 27, FAO Rome,
1975   pp. 253-271.

Elgala A.M. and Schlichting E. Der Einfluss von Huminsäure- und DTPA-Zusatz auf die
1976   Extrahiernarkeit von Fe, Mn, Zn und Cu aus gedüngten und ungedüngten Böden.
            Landw. Forschung 29:34-41.

Elliot L.F. and Blaylock J.W. Effects of wheat straw and alfalfa amendments of
1975   solubilization of manganese and iron in soil. Soil Sci. 120:205-211.

Ellwardt P.C. The alteration of content of polycyclic aromatic hydrocarbons in soils and
1976   plants by using sludge and waste compost in agriculture. (In press)

Elmund G.K., Morrison S.M., Grant D.W. and Nevins M.P. Role of excreted chlor-
1971   tetracycline in modifying the decomposition process in feedlot waste. Bull.
            Environmental Contamination and Technology 6 (2):129-132.

FAO Soils Bulletin 27. Organic materials as fertilizers. Report of the FAO/SIDA Expert
1975   Consultation, Rome 2-6 December 1974. FAO Rome. 394 p.

Farmer V.C. and Morrison R.I. Lignin in sphagnum and phragmites and in peats derived
1964   from these plants. Geochim. Cosmochim. Acta 28:1537-1546.

Filip Z., Haider K., Beutelspacher H. and Martin J.P. Comparisons of IR-Spectra from
1974   melanins of microscopic soil fungi, humic acids and model phenol polymers.
            Geoderma 11:37-52.

Filip Z., Haider K., Flaig W., Beutelspacher H., Küster E. and Martin J.P. Einfluss
1971   der Tonminerale auf die Huminstoffbildung einiger Bodenpilze. Landbauforsch.
            Völkenrode 21:97-102.

Filip Z., Haider K. and Martin J.P. Influence of clay minerals on growth and metabolic
1971a   activity of Epicoccum nigrum and Stachybotrys chartarum. Soil Biol. Biochem.
            4:135-145.

Filip Z., Haider K. and Martin J.P. Influence of clay minerals on the formation of humic
1971b   substances by Epicoccum nigrum and Stachybotrys chartarum. Soil Biol.
            Biochem. 4:147-154.

Flaig W. Contribucion al estudio de los acidos huminicos. Monografias de Ciencia
1955   Moderna Nr. 46:1-167.

Flaig W. Chemie der Humusstoffe. Suomen Kemistilehti, A 33:229-251.
1960a

Flaig W. Comparative chemical investigations on natural humic compounds and their model
1960b   substances. Sci. Proc. Roy. Dublin Soc. ser. A 1, 4:149.

Flaig W. Zur Umwandlung von Lignin in Humusstoffe. Freiberger Forschungshefte A
1962   254:39-56.

Flaig W. Humusstoffe. Handbuch der Pflanzenernährung und Düngung, Bd. II: Boden und
1966   Düngemittel, Springer-Verlag, Wien, pp. 282-458.

Flaig W. Uptake of organic substances from soil organic matter by plant and their
1968   influence on metabolism. Pontificiae Acad. Scient. Scripta Varia 32:723-770.

Flaig W. Organic compounds in soil. Soil Sci. 111:19-33.
1971

Flaig W. Slow releasing nitrogen fertilizer from the waste product, lignin sulphonates.
1973   Chemistry and Industry p. 553-554.

Flaig W. and Beutelspacher H. Physikalische Chemie der Huminsäuren. Landbouwk.
1954   Tijdschr. 66:306-336.

Flaig W. and Otto H. Zur Kenntnis der Huminsäuren (III. Mitteilung). Untersuchungen
1951   über die Einwirkungen einiger Chinone als Modellsubstanzen der Auf- und
         Abbauprodukte von Huminsäuren sowie einiger Redoxsubstanzen auf das Wachstum
         von Pflanzenwurzeln. Landw. Forschung 3:66-89.

Flaig W. and Haider K. Reaktionen mit oxydierenden Enzymen aus Mikroorganismen.
1961   Planta Medica, Z. f. Arzneipflanzenforsch. 9:123-139.

Flaig W. and Riemer H. Polarographische Untersuchungen zum Verhalten von Trihydroxy-
1971   toluolen bei der Reaktion mit Glycin unter oxydierenden Bedingungen. Justus
         Liebig Annakeb der Chemie 746:81-85.

Flaig W. and Söchtig H. Einige Grundlagen zur Frage der Krümelbildung. Landbauforsch.
1957   7:80-83.

Flaig W. and Söchtig H. Organische Verbindungen als Stickstoffquelle für die Ernährung
1967   der Pflanzen. Anales de Edafologia y Agrobiologia XXVI:801-818.

Flaig W. and Söchtig H. About the influence of phenolic peat constituents on metabolism of
1972   plant. Proc. 4th Int. Peat Congr. 4:19-30. Otaniemi, Finland.

Flaig W. and Söchtig H. Wirkung organischer Bodensubstanzen und Ertragssicherung.
1973   Landbauforschung Völkenrode 23:19-28.

Flaig W. and Söchtig H. Ein Beitrag zur umweltfreundlichen Technik durch Verwertung
1974   der Sulfitablaugen der Zellstoffindustrie als organischer Stickstoffdünger.
         Neth. J. Agric. Sci. 22:255-261.

Flaig W., Beutelspacher H. and Rietz E. Chemical composition and physical properties
1975   of humic substances. In: Soil Components 1, Organic Components. J.E.
         Gieseking (Ed), Springer-Verlag, New York, Heidelberg, Berlin. p. 1-211.

Flaig W., Beutelspacher H. and Söchtig H. Zur Chemie der anorganischen und organischen
1958   Komponenten der Krümelbildung. Tagungsberichte No. 13, Probleme der
         Krümelstabilitätsmessung, Deutsche Akademie der Landbauwissenschaften zu
         Berlin. p. 225-244.

Flaig W., Beutelspacher H. and Söchtig H. Ein Beitrag aus dem Bereich der molekularen
1962   Dimension zur Morphologie des Bodens. Z. Pflanzenernähr., Düng. und Boden-
         kunde 98:225-231.

Flaig W., Schobinger U. and Deuel H. Umwandlung von Lignin in Huminsäuren bei der
1959   Verrottung von Weizenstroh. Chem. Ber. 92:1973-1982.

Flaig W., Söchtig H. and Beutelspacher H. Einfluss der Humusstoffe auf die Umtauschkapa-
1963   zität der Böden. Landbauforsch. Völkenrode 13:13-20.

Freudenberg K. Forschung am Lignin. Fortschr. Chem. Org. Naturstoffe 20:41-72.
1962

Freudenberg K. Entwurf eines Konstitutionsschemas für das Lignin der Fichte. Holzforsch.
1964a   18:3-9-

Freudenberg K. Ergänzung des Konstitutionsschemas für das Lignin in der Fichte.
1964b   Holzforsch. 18:166.

Führ F. and Sauerbeck D. Uber die Aufnahme und Translokation ^{14}C-markierter
1964   organischer Rotteprodukte bei Raphanus sativus. z. Pflanzenernähr., Düng.,
        Bodenk., 105:136.

Führ F. and Sauerbeck D. Die räumliche und chemische Verteilung durch die Wurzel
1965   aufgenommener organischer Rotteprodukte bei Dancus carota. Z. Landw.
        Forsch. 19: Sonderheft 153-163.

Führ F. and Sauerbeck D. The uptake of straw decomposition products by plant roots.
1966   In: The Use of Isotopes in Soil Organic Matter Studies. Report of the FAO/
        IAEA Techn. Meeting. Pergamon, Oxford. p. 73-83.

Führ F. and Sauerbeck D. The uptake of colloid organic substances by plant roots as
1967   shown by experiments with ^{14}C-labelled humus compounds. In: Use of Isotopes
        and Plant Nutrition. FAO/IAEA Vienna. p. 317.

Führ F. and Sauerbeck D. Decomposition of wheat straw in the field as influenced by
1968   cropping and rotation. In: Isotopes and Radiation in Soil Organic Matter Studies.
        IAEA Vienna. p. 241-250.

Fustec-Mathon E., Haider K. and Martin J.P. Participation à la formation des composés
1973   humiques du sol de phénols microbiens synthétisés à partir d'hydrates de
        carbone. C.R. Acad. Sc. Paris, 276 Série D:929-932.

Galstian A.S. Fermentative activity of the soils of Armenia. Yerevan Publishing House,
1974   Ajastan.

Garg A.C., Idnani M.A. and Abraham T.P. Organic manures. ICAR Tech. Bull. (Agric.)
1971   32. Indian Council of Agricultural Research, New Delhi.

Gieseking J.E. (Ed). Soil Components, Vol. 1 Organic Components. Springer-Verlag,
1975   New York, Heidelberg, Berlin. 534 p.

Gilbert F.A. Copper in nutrition. Adv. Agron. 4:147-177.
1952

Golueke C.G. Composting. Rodale Press, Emmaus, Pennsylvania.
1973

Gorbunow N.I. The absorption capacity of soils and its nature. Sel Khozgiz.
1948

Gordon M. and Springer E. Wachstumsversuche mit 4 botanisch unterschiedlichen
1964   Spagnumtorfeb zu 8 verschiedenen Kulturen. Torfnachrichten 15:1.

Grabbe K. and Haider K. Die Huminstoffbildung und die Stickstoffverteilung bei der
1971   Strohrotte in Beziehung zur mikrobiellen Phenolbildung. Z. Pflanzener.,
        Bodenkunde. 129:202-216.

Graham E.R. Availability of natural phosphates according to energy changes. Soil Sci.
1955   Soc. Amer. Proc. 19:26-29.

Graham-Bruce I.J. Adsorption of disulfoton by soil. J. Sci. Fd. Agric. 18:72-77.
1967

Greenland D.J. and Oades J.M. Saccharides. In: Soil Components 1, Organic Components.
1976   J.E. Gieseking (Ed), Springer-Verlag, New York, Heidelberg, Berlin. p. 213-261.

Grunes D.L. and Krantz B.A. Nitrogen fertilization increases N, P and K concentrations
1958 in oats. Agron. J. 50:729-732.

Guckert A., Cure B. and Jacquin F. Comparative evolution of the polysaccharides of the
1971 humin after incubation of 14C-glucose and 14C-straw. Trans. Int. Symp.
 Humus et Planta V, Prague, September 1971. p. 155-160.

Guenzi W.D. and McCalla T.M. Phytotoxic substances extracted from soil. Soil Sci.
1966 Soc. Amer. Proc. 30:214-216.

Guminski S. and Guminska Z. Neue Untersuchungen über den Mechanismus der Humuswirt-
1953 schaft auf die Pflanze. (Polish). Acta Soc. Bot. Polon. 22:45-63.

Haider K. Untersuchungen über den mikrobiellen Abbau von Lignin. Zbl. Bakteriol.
1966 Parasitenkunde Infektionskrankh. und Hygiene 198:308-316.

Haider K. and Martin J.P. Synthesis and transformation of phenolic compounds by
1967 Epicoccum nigrum in relation to humic acid formation. Proc. Soil Sci. Soc.
 Amer. 31(6):766-772.

Haider K. and Martin J.P. The role of microorganism in the formation of humic acids.
1968 In: Isotopes and Radiation in Soil Organic Matter Studies. IAEA Vienna. p. 189-195

Haider K. and Martin J.P. Humic acid-type phenolic polymers from Aspergillus sydowi
1970 culture medium, Stachybotrys spp. cells and autoxydized phenol mixtures. Soil
 Biol. Biochem. 2:145-156.

Haider K., Filip Z. and Martin J.P. Action of clay minerals on different metabolic
1971 processes of soil fungi. Studies about humus. Trans. Int. Symp. Humus et
 Planta V, Prague, September 1971. pp. 55-66.

Haider K., Filip Z. and Martin J.P. Einfluss von Montmorillonit auf die Bildung von
1970 Biomasse und Stoffwechselzwischenprodukte durch einige Mikroorganismen.
 Arch. Mikrob. 73:201-215.

Haider K., Martin J.P., Filip Z. and Fustec-Mathon E. Contribution of soil microbes to
1975 the formation of humic compounds. Proc. Int. Meet. Humic Substances,
 Nieuwersluis, Netherlands Centre for Agricultural Publishing and Documentation
 (PUDAC), Wageningen. p. 71-85.

Haider K., Frederick L.R. and Flaig W. Reactions between amino acid compounds and
1965 phenols during oxydation. Pl ant and Soil XXII:49-64.

Haider K., Lim S. and Flaig W. Untersuchungen über die Einwirkung von Mikroorganismen
1962 auf 14C-markierte phenolische Verbindungen. Landw. Forsch. 15:1-9.

Haider K., Lim S. and Flaig W. Experimente und Theorien über den Ligninabbau bei der
1964 Weissfäule des Holzes und bei der Verrottung pflanzlicher Substanz im Boden.
 Holzforsch. 18:81-88.

Hance R.J. The adsorption of linuron, atrazine and EPTC by model aliphatic adsorbents
1969 and soil organic preparations. Weed Res. 9:108-113.

Harms H. Uber die quantitative Bestimmung der Aufnahme von Phenolcarbonsäuren durch
1968 die Wurzel von Weizenkeimpflanzen. Mitt. Dtsch. bodenkdl. Ges. 8:159-161.

Harms H. Positionsspezifische o-Demethylierung von Benzoesäuren in Zellsuspensions-
1972 kulturen sowie in Weizenkeimpflanzen. Hoppe Seyler's Z.G. Physiol. Chemie
 353:1523.

Harms H., Söchtig H. and Haider K. Untersuchungen zur Aufnahme und Umwandlung [14]C-
1969a   markierter Phenole durch die Pflanze. I. Aufnahme von ^{14}C-carboxylmarkierter
         p-Hydroxybenzoe-, Vanillin- und Syringasäure durch die Wurzeln von Weizen-
         keimpflanzen und Vetieilung der Aktivität über die Pflanze. Plant and Soil
         XXXI (1):129-142.

Harms H., Söchtig H. and Haider K. Untersuchungen zur Aufnahme und Umwandlung [14]C-
1969b   markierter Phenole durch die Pflanze. II. Die Umwandlung von p-Hydroxybenzoe-
         säure, Vanillinsäure sowie Syringsäure nach der Aufnahme durch die Wurzel von
         Weizenkeimpflanzen. Plant and Soil XXXI(2):257-272.

Harms H., Söchtig H. and Haider K. Aufnahme und Umwandlung von in unterschiedlichen
1971   Stellungen ^{14}C-markierten Phenolcarbonsäuren in Weizenkeimpflanzen. Z.
         Pflanzenphysiol. 64:437-445.

Harms H., Haider K., Berlin J., Kiss P. and Barz W. Uber o-Demethylierung und Decarb-
1972   oxylierung von Benzoesäuren in pflanzlichen Zellsuspensionskulturen. Planta
         105:342-351.

Hartmann W.J. An evaluation of land treatment of municipal wastewater and physical siting
1975   of facility installations. U.S. Department of the Army, Washington D.C.

Hofmann E. and Hoffmann G. Die Bestimmung der Biologischen Tätigkeit in Boden mit
1966   Enzymmethoden. Adv. Enzymol. 28:365-378.

Hobbs J.A. and Brown P.L. Nitrogen changes in cultivated dryland soils. Agron J. 49:
1957a   257-260.

Hobbs J.A. and Brown P.L. Nitrogen and organic carbon changes in cultivated Western
1957b   Kansas soils. Kans. Agric. Exp. Sta. Tech. Bull. 89.

Holmes R.S. and Brown J.G. Chelates as correctives for chlorosis. Soil Sci. 80:167-179.
1955

Hupkens van der Elst F. Nutrient requirements for establishment and maintenance of good
1972   pastures on high moor peat soils in New Zealand. Proc. 4th Int. Peat Congress,
         Otaniemi, Finland. p. 21.

Humus et Planta. Studies about Humus. Trans. Int. Symp. I-VI, Prague, 1961, 1963,
         1965, 1967, 1971, 1975.

International Atomic Energy Agency. The use of isotopes in soil organic matter studies.
1966   Report of the FAO/IAEA Tech. Meeting in cooperation with the International
         Soil Science Society, Braunschweig-Völdenrode, 9-14 September 1963.
         Pergamon, Oxford. 271 p.

International Atomic Energy Agency. Isotopes and radiation in soil organic matter studies.
         Proc. Symp. 15-19 July 1968. IAEA Vienna. 584 p.

Jagnow G. The effect of altitude, precipitation and cultivation on the organic carbon and
1971   nitrogen content of East African soils. Trans. Int. Symp. Humus et Planta V,
         Prague. 381 p.

Jaiswal P.L. (Ed). Handbook of manures and fertilizers. Indian Council of Agricultural
1971   Research, New Delhi. 96 p.

Jansson S.L. Tracer studies on nitrogen transformation in soils with special attention to
1958   mineralization-immobilization relationships. Kungl. Lantbrukshogsk. Am.
         10:101-126.

Jansson S.L., Hallam M.J. and Bartholomew W.V. Preferential utilization of ammonium
1955   over nitrate by microorganisms in the decomposition of oat straw. Plant and
          Soil 6:382-390.

Jansson S.L. and Person J. Co-ordination of humus chemistry and soil organic matter
1968   studies. IAEA Vienna. p. 111-123.

Jenkinson D.S. The turnover of organic matter in soil. In: The Use of Isotopes in Soil
1966a   Organic Matter Studies. Report of the FAO/IAEA Tech. Meeting. Pergamon,
          Oxford. p. 187-197.

Jenkinson D.S. The priming action. In: The Use of Isotopes in Soil Organic Matter
1966b   Studies. Report of the FAO/IAEA Tech. Meeting. Pergamon, Oxford. p. 199-208

Jenkinson D.S.   Experimental techniques for using carbon-14 in studies of soil organic
1966c   matter. In: The Use of Isotopes in Soil Organic Matter Studies. Report of the
          FAO/IAEA Tech. Meeting. Pergamon, Oxford. p. 365-369.

Jenkinson D.S. Studies on the decomposition of plant materials in soil, I-III. J. Soil Sci.
          16:104-115 (1965); 17:280-302 (a966d); 19:25-39 (1968).

Jenkinson D.S. Studies on the decomposition of ^{14}C-labelled organic matter in soil. Soil
1971   Sci. 111:64-70.

Jenny H. Factors of soil formation. McGraw-Hill, New York. 281 p.
1941

Jenny H. Mo. Agric. Exper. Stat. Bull..324:1-10

Jenny H. and Raychaudhuri S.P. Effect of climate and cultivation on nitrogen and organic
1960   matter reserves in Indian soils. Publ. Indian Council of Agricultural Research,
          New Delhi.

Kaila A. Humification of straw at various temperatures. Acta Agral. Fenn. Helsinki 78:
1952   3-32.

Kastori R., Harms H., Söchtig H. and Haider K. Untersuchungen zur Aufnahme und
1970   Umwandlung C^{14}-markierter Phenole durch die Pflanze. III. Die Aufnahme, der
          Transport und die Umwandlung von C^{14}-markiertem Thymohydrochinon durch
          Weizenkeimpflanzen. Plant and Soil 33:597-611.

Kelley W.P. and Jenny H. The relation of crystal structure to base-exchange and its
1936   bearing on base-exchange in soils. Soil Sci. 41:367-382.

Kellogg C.E. Potentialities and problems of arid soils. Desert Res. Proc. Int. Symp.
1953

Khan S.U. and Schnitzer M. The potassium permanganate oxidation of methylated and
1971   unmethylated humic acids extracted from solonetz, solod and chenozem A_H
          horizons. Isr. J. Chem. 9:667-677.

Khanna K.L. and Roy P.K. Studies on factors affecting soil fertility in the sugar belt of
1956   Bihar: VII. Influence of organic matter on phosphate solubility under calcareous
          soil conditions. J. Indian Soc. Soil Sci. 4:189-192.

Kick H. Die Anwendung von Müllkomposten und Müllklärschlammkomposten in der Land-
1971   wirtschaft. Hdb. Müll- und Abfallbeseitigung 6710. Schmidt Verlag Berlin.

Kick H., Sauerbeck D. and Führ F. Die Aufnahme von Kohlendioxid durch die Pflanzenwur-
1965   zel. II Untersuchungen zur Verteilung innerhalb der Pflanze. Plant and Soil 22:
          99-111.

Kononova M.M. Soil organic matter, its nature, its role in soil formation and in soil
1966   fertility. Pergamon, Oxford.

Kononova M.M. Humus of virgin and cultivated soils. In: Soil Components 1, Organic
1975   Components. J.E. Gieseking (Ed), Springer-Verlag, New York, Heidelberg,
          Berlin. p. 475-526.

Kononova M.M. and Alexandrova I.V. Formation of humic acids during the plant residue
1973   humification and their nature. Geoderma 9:157-164.

Kubiena W. Entwicklingslehre des Bodens. Springer-Verlag, Wien. 215 p.
1948

Kubiena W. Soils of Europe. Thomas Murby, London. 317 p.
1953

Kumada K. and Suzuki A. Isolation of anthraquinone from humus. Nature 191:415-416.
1961   London.

Kuprevich V.F. and Shcherbakova T.A. Soil enzymes. National Technical Information
1971   Service Document TT 69 - 53048, Springfield Va. (translated from Russian)

Kurki M. On the fertility of cultivated bogs in Finland. In: Proc. 4th Int. Peat Congress,
1971   Otaniemi, Finland. p. 37.

Lambert E.N., Seafort C.E. and Ahmed N. The occurrence of 2-methoxy-1,4-naphtho-
1971   quinone in Caribbean verti soils. Soil Sci. Soc. Amer. Proc. 35:463-464.

Lenvain J. and De Boodt M. The effect of small quantities of hydrophobic soil conditioner
1975   on the decrease of evaporation and the beneficial development of Vetiveria
          zizanoides (L.) stapf. in the wet tropics. Proc. 3rd Int. Symp. on Soil
          Conditioning. Ghent, 1975. 464 p.

Lindsay W.L. and Norell W.A. Equilibrium relationships of Zn^{2+}, Fe^{3+}, Ca^{2+} and H^+
1969   with EDTA and DTPA in soils. Soil Sci. Soc. Amer. Proc. 33:62-68.

Loer C.R. Animal waste management with nutrient control. In: K.S. Porter (Ed)
1975   Nitrogen and Phosphorus. Ann Arbor Science. p. 216-269.

Maeder H. Chemische und Pflanzenphysiologische Untersuchungen mit Rottestroh. Diss.
1960   Justus Liebig Universität Giessen.

Mann P.J.G. and Quastel J.H. Manganese metabolism in soils. Nature 158:154-156.
1946   London.

Martin J.P. and Haider K. Phenolic polymers of Stachybotrys atra, Stachybotrys
1969   chartarum and Epicoccum nigrum in relation to humic acid formation. Soil Sci.
          107:260-270.

Martin J.P. and Haider K. Microbial activity in relation to soil humus formation. Soil
1971   Sci. 111:54-63.

Martin J.P., Haider K. and Bondietti E. Properties of model humic acids synthesized by
1975   phenoloxidase and autoxidation of phenol and other compounds formed by soil
          fungi. Proc. Int. Meet. Humic Substances, Nieuwersluis. PUDAC, Wageningen.
          p. 171-186.

Martin J.P., Richards S.J. and Haider K. Properties and decomposition and binding action
1967   action in soil of "humic acids" synthesized by Epicoccum nigrum. Soil Sci. Soc.
          Amer. Proc. 31:657-662.

Martin J.P., Haider K. and Saiz Jimenez C. Sodium amalgam reductive degradation of
1974   fungal phenolic polymers, soil humic acids and simple phenolic compounds. Soil
            Sci. Soc. Amer. Proc. 38:760-765.

Martin J.P., Haider K. Farmer W.J. and Fustec-Mathon E. Decomposition and distribution
1974   of residual activity of some ^{14}C-microbial polysaccharides and cells, glucose,
            cellulose and wheat straw in soil. Soil Biol. Biochem. 6:221-230.

Mather E. and Hart J.F. The geography of manure. Land Economics 32(1):25-38.
1956

Mathur S.P. Characterization of soil humus through enzymatic degradation. Soil Sci.
1971   111:147-157.

Mattson S. and Koutler-Andersson E. The acid base condition in vegetation, litter and
1942   humus: V. Products of partial oxidation and ammonia fixation. Kundg. Lant-
            brukshogsk. Am. 10:284-332.

Mayaudon J. and Simonart P. Etude de la décomposition de la matière organique dans le
1958   sol au moyen de carbone radioactif. 1. Décomposition du glucose radioactif dans
            le sol. A. Repartition de la radioactivité dans fractions humiques du sol. Plant
            and Soil IX:376-380.

Mayaudon J. and Simonart P. Etude de la décomposition de la matière organique dans le
1959a   sol au moyen de carbone radioactif. III. Décomposition des substances solubles
            dialysables des proteines et des hemicelluloses. Plant and Soil XI:170.

Mayaudon J. and Simonart P. Etude de la décomposition de la matière organique dans le
1959b   sol au moyen de carbone radioactif. V. Décomposition de cellulose et de lignie.
            Plant and Soil XI:181-192.

Mayaudon J. and Simonart P. Stabilité de l'humus du sol etudiée à l'aide d'humus marqué
1960   au ^{14}C-Arch. Intern. de Phys. et de Biochim. 68:512.

Mayaudon J. and Simonart P. Decomposition of cellulose ^{14}C and lignon ^{14}C in the soil.
1961   Ecology of Soil Fungi.

Mayaudon J. and Simonart P. Humification des microorganismes marqués par ^{14}C dans le
1963   sol. Anales de l'Inst. Pasteur 105:257-266.

McGrath D. Hydroxyanthraquinones in soils. Geoderma 7-8:168-176.
1972

McLaren A.D. Soil as a system of humus and clay immobilized enzymes. Chemica
1975   Scripta 8:97-99.

McLaren A.D. and Peterson G.H. (Eds). Soil biochemistry, Vol.1. Marcel Dekker, New
1967   York. 509 p.

McLaren A.D. and Skuljins J. (Eds). Soil biochemistry, Vol. 2. Marcel Dekker, New
1971   York. 527 p.

Mietinen J.K. Assimilation of amino acids in higher plants. Symp. Soc. Experimental
1959   Biology III. Utilization of Nitrogen and its Compounds by Plants. p. 210-229.

Mitscherlich E.A. An der Grenze der Ertragssteigerung. Z. Pflanzenernähr., Düng.,
1948   Bodenkunde 40:193-200.

Möller U. Uberlegungen zur Wahl und Kombination verschiedener Verfahren bei der
1971   Schlammbehandlung. Schriftenreihe "Gewässerschutz-Wasser-Abwasser",
            Bd. 6:325-359. Aachen.

Mohtadi S. Beitrag zur Isolierung von pflanzenphysiologisch wirksamen Stoffen während
1962   der Rotte von Stroh. Dissertation Giessen.

Mortland M.M. and Wolcott R. Sorption of inorganic nitrogen compounds by soil material.
1965   In: Agron. Monograph 10: Soil Nitrogen. p. 151-197. Amer. Soc. Agron.,
        Madison, Wisconsin.

Morrison R.I. Products of the alkaline nitrobenzene oxidation of soil organic matter.
1963   J. Soil Sci. 14:201-216.

Motomura S. The relationship between ferrous iron formation and nitrogen metabolism.
1962   Soil Sci. and Plant Nutr. 8:9-17.

Musso H., Gizycki U.V., Kramer H. and Dopp H. Uber Orceinfarbstoff. XXIV. Uber
1965   den Autooxydations-mechanismus bei Resorcinderivaten. Chem. Ber. 98:3952-3963.

Naucke W., Laaser H.V. and Tarkmann F. New chemical investigations on watersoluble
1972   organic substances in low decomposed sphagnum peats. Proc. 4th Int. Peat
        Congr., Otaniemi, Finland 4:45-60.

Nehring K. and Schiemann R. Untersuchungen zum Humusproblem. I. Mitt. Beiträge zur
1952   Kenntnis der Vorgänge bei der Rotte von Stallmist und Komposten sowie zur
        Kenntnis der Humins'äuren. Z. Pflanzernernährung., Düng., Bodenkunde 57:
        97-113.

Oberländer H.E. and Roth K. Transformation of ^{14}C-labelled plant material in soils under
1968   field conditions. In: Isotopes and Radiation in Soil Organic Matter Studies.
        IAEA, Vienna. p. 251-264.

Ogner G. and Schnitzer M. Chemistry of fulvic acid, a soil humic fraction, and its
1971   relation to lignin. Canad. Journ. Chem. 49:1053-1063.

Okuda A. and Hori S. Studies on the effect of humic acid on availability of phosphorus.
1957   Soil and Plant Food 2:195-197.

Olteanu G.H. and Brad I. Contributii privind continutul in aminoacizi, zaharuri, acizi
1969   organic si substante aromatice la soiuri de cartof cu rezistenta diferita fata de
        mana. Cartoful, Annalele, L.C.C.A., Vol. I S. 177-184 (Romanian)

Orlov D.S. Humic acid in soils. Moscow University. pp. 331 (Russian)
1974

Orlov D.S. and Gorskova E.I. Grösse und Gestalt der Huminsäurepartikel aus Schwarz-
1965   erde und Rasenpodsolböden. Nauchenye doklady vyssej skoly Biologieskie nauki
        Moskva 1:207-212.

Parsons J.W. and Tinsley J. Nitrogenous substances. In: Soil Components 1, Organic
1975   Components. J.E. Gieseking (Ed), Springer-Verlag, New York, Heidelberg,
        Berlin. p. 263-304.

Paul E.A. and McLaren A.D. (Eds). Soil Biochemistry Vol. 3. Marcel Dekker, New
1975a   York. 334 p.

Paul E.A. and McLaren A.D. (Eds). Soil Biochemistry Vol. 4. Marcel Dekker, New
1975b   York. 277 p.

Perkins H.F. and Purvis E.R. Soil and plant studies with chelates of ethylenediamine
1954   tetraacetic acid. Soil Sci. 78:325-330.

Philips M. The chemistry of lignin. Chem. Rev. 14:103-170.
1934

Piper C.S. The availability of manganese in the soil. J. Agric. Sci. 21:762-779.
1931

Piper T.J. and Posner A.M. Sodium amalgam reduction of humic acid. 1. Evaluation of
1972a   the method. Soil Biol. Biochem. 4:513-523.

Piper T.J. and Posner A.M. Sodium amalgam reduction of humic acid. II. Application of
1972b   the method. Soil Bio. Biochem. 4:525-531.

Pontificiae Academiae Scientiarum Scripta Varia. Study week on soil organic matter and
1968   soil fertility. 1017 p.

Pound E.C., Crites R.W. and Thomas R.E. Wastewater treatment and reuse by land
1973   application. U.S. Environmental Protection Agency, Washington D.C.

Povoledo D. and Golterman H.L. (Eds). Humic substances: their structure and function
1975   in the biosphere. Proc. Int. Meeting Humic Substances, Nieuwersluis, Nether-
       lands, 29-31 May 1972. PUDAC, Wageningen. 368 p.

Prat S. Das Problem des Eindringens und der Einwirkung von Humusstoffen auf die
1963a   Pflanzenzellen. Intern. Torfkongress, Leningrad, USSR, Nr. 3806.

Prat S. Permeability of plant tissues to humic acids. Biol. Plant 5:279.
1963b

Pratt P.F. Worldwide nitrogen fixation estimated. Chem. Eng. News 54:34.
1976

Pratt P.F., Broadbent F.E. and Martin J.P. Using organic wastes as nitrogen fertilizers.
1973   California Agriculture 27(6):10-13.

Puustjärvi V. Peat in horticulture. In: Soils Bulletin 27, FAO Rome. p. 133-145.
1975

Rabochev I.S. Methods of studying mineralogical composition and organic matter of soils.
1975   YLYM Publishing House. 415 p.

Rayment A.F. The influence of initial and maintenance fertilizers on the growth and ecology
1972   of grasscover mixtures on a Newfoundland peat soil. In: Proc. 4th Int. Peat
       Congress, Otaniemi, Finland. p. 111.

Rennie D.A., Truog E. and Allen O.N. Soil aggregation as influenced by microbial gums.
1954   Level of fertility and kind of crop. Soil Sci. Soc. Amer. Proc. 18:399-403.

Reinhardt G. Untersuchungen über die Einwirkungen von Lignin und dessen Abbauprodukten
1961   auf das Wachstum und den Stoffwechsel von Pflanzen. Dissertation Universität
       Giessen.

Ritter G.J., Seborg R.M. and Mitchell R.L. Factors affecting quantitative determination
1932   of lignin by 72 percent sulfuric acid method. Ind. Eng. Chem. Analyt. Edit. 4:
       202.

Rotini O.T. and Sequi P. Progrès réalisés dans la fertilité du sol et la nutrition des
1974   plantes. Geoderma 12:331-346.

Saalbach E. Zur Kenntnis der Huminsäuren, CIV. Mitt. Einfluss von Modell-Substanzen
1957   von Humusstoffen auf den Stoffwechsel von Getreide. Landw. Forsch. 9.
       Sonderheft 95-100.

Saiz-Jiminez C., Haider K. and Martin J.P. Anthraquinones and phenols as intermediates
1975   in the formation of dark-colored, humic acid-like pigments by Eurotium
            echinulatum. Soil Sci. Soc. Amer. Proc. 39:649-653.

Sauerbeck D. Die Umsetzung markierter organischer Substanzen im Boden in Abhängigkeit
1968a   von Art, Menge und Rottegrad. Landw. Forsch. 21:91-102.

Sauerbeck D. Stability of recently formed humus compounds in soil. In: Isotopes and
1968b   Radiation in Soil Organic Matter Studies. IAEA, Vienna. p. 57-66.

Sauerbeck D. Comparison of plant material and animal manure in relation to their
1968c   decomposition in soil. In: Isotopes and Radiation in Soil Organic Matter Studies.
            IAEA. Vienna. p. 219-225.

Sauerbeck D. and Führ F. Alkali extraction and fractionation of labelled plant material
1968   before and after decomposition: a contribution to the technical problems in
            humification studies. In: Isotopes and Radiation in Soil Organic Matter Studies.
            IAEA, Vienna. p. 3-11.

Sauerbeck D. and Führ F. The interference of carbon-14 labelled carbon dioxide in studies
1966   on the uptake of organic substances by plant roots. In: The Use of Isotopes in
            Soil Organic Matter Studies. Report of the FAO/IAEA Tech. Meeting. Pergamon,
            Oxford. p. 61-72.

Sauerbeck D. and Führ F. Die Umsetzung von markiertem Pflanzenmaterial im Boden unter
1970   Feldbedingungen. Mitt. Deutsche Bodenkundl. Gesellsch. 10:174-177.

Sauerlandt W. and Tietjen C. Humuswirtschaft des Ackerbaues. DLG-Verlag, Frankfurt/
1970   Main. 239 p.

Sax K. The stimulation of plant growth by ionising radiation. Radiation Botany 3:179-186.
1963

Scarsbrook C.E. Nitrogen availability. In: Soil Nitrogen, Agron. Monograph 10, Amer.
1965   Soc. Agron., Madison, Wisconsin. p. 486-507.

Schanderl H. Botanische Bakteriologie und Stickstoffhaushalt der Pflanzen auf neuer
1947   Grundlage. Verlag Ullmer Stuttgart. 198 p.

Scharpenseel H.W. Herstellung und Reinigung von titriummarkierten Grau- und Braun-
1960a   Huminsäurepräparaten sowie von Titrium-Pupurogallin. Z. Pflanzenernähr.,
            Düng. und Bodenkunde 91:131-146.

Scharpenseel H.W. Untersuchungen mit radioaktiv markierten Huminsäuren und Vorstufen.
1960b   2. Teil. Z. Pflanzenernähr., Düng. und Bodenkunde 91:193-202.

Scharpenseel H.W. Labelling of soil organic matter. In: The Use of Isotopes in Soil
1966   Organic Matter Studies. Report of the FAO/IAEA Tech. Meeting. Pergamon,
            Oxford. p. 351-364.

Scharpenseel H.W. Aufbau und Bindungsform der Ton-Huminsäurekomplexe. Teil IV.
1970   Z. Pflanzenernähr., Düng. und Bodenkunde 55:151-169.

Scharpenseel H.W. and Beckmann H. Untersuchungen zur Kohlendioxid-Entbindung des
1964   Bodens. II. Teil. Spezielle Studien unter Verwendung radioactiver Tracer.
            Z. Pflanzenernähr., Düng. und Bodenkunde 104:110-119.

Scharpenseel H.W. and Krause R. Aminosäureuntersuchungen an verschiedenen organizchen
1962   Sedimenten, besonders Grau- und Braunhumins'äurefraktionen verschiedener
            Bodentypen (einschliesslich ^{14}C-markierter Huminsäuren). Z. Pflanzenernähr.,
            Düng. und Bodenkunde 96:11-34.

Scheffer F. and Ulrich B. Lehrbuch der Agrikulturchemie und Bodenkunde, III. Teil
1960   Humus und Humusdüngung 1, Enke Stuttgart. 266 p.

Schenkel W. Waste - classification, types and quantities. Conference at the International
1973   Trade Fair on Waste Handling, Avall 73, Jönköping, Sweden, 27-31 August 1973.

Schlichting E. Kupferbindung und -fixierung durch Humusstoffe. Acta Agric. Scand. 5:
1955   313.356.

Schneider S. Verteilung der Moore auf der Erde. In: Moor- und Torfkunde, E.
1976   Schweizerbart'sche Verlagsbuchhandlung, Stuttgart. p. 27-40.

Schnitzer M. and Desjardins J.G. Carboxyl and phenolic hydroxyl groups in some organic
1965   soils and their relation to the degree of humification. Can. J. Soil. Sci. 45:
            257-264.

Schnitzer M. and Khan S.U. Humic substances in the environment. Marcel Dekker, New
1972   York. 327 p.

Schobinger U. Chemische Untersuchungen über die Umwandlung von Weizenstrohlignin im
1958   Laufe der Verrottung. Dissertation ETH Zürich.

Schöllhorn R. and Burris R.H. Study of intermediates in nitrogen fixation. Federation
1966   P roc. 24:710.

Simonart P. and Mayaudon J. Etude de la d écomposition de la matière organique dans le
1958a   sol au moyen de carbone radioactif. I. Cinetique de l'oxydation en CO_2 de divers
            substracts radioactifs. Plant and Soil 9:367-375.

Simonart P. and Mayaudon J. Etude de la d écomposition de la matière organique dans le
1958b   sol au moyen de carbone radioactif. II. Décomposition du glucose radioactif
            dans le sol. B. Repartition de la radioactivité dans l' α-humus. Plant and Soil
            9:381-384.

Simonart P. and Mayaudon J. Etude de la décomposition de la matière organique dans le
1959   sol au moyen de carbone radioactif. III. Décomposition des substances solubles
            des proteines et hemicelluloses. Plant and Soil 11:170-175.

Simonart P., Mayaudon J. and Batistic L. Etude de la décomposition de la matière
1959   organique dans le sol au moyen de carbone radioactif. IV. Décomposition des
            pigments foliares. Plant and Soil 11 (2):176-180.

Simonart P. and Mayaudon J. Etude des transformations de la matière de sol au moyen du
1966   carbone-14. In: The Use of Isotopes in Soil Organic Matter Studies. Report
            of the FAO/IAEA Tech. Meeting. Pergamon, Oxford. p. 245-258.

Simonson R.W. Outline of a generalized theory of soil genesis. Soil Sci. Soc. Amer.
1959   Proc. 23:152-156.

Skujins J.J. Enzymes in soil. In: Soil Biochemistry 3. A.D. McLaren and G.H.
1967   Peterson (Eds), Marcel Dekker, New York.

Smith F.B., Stevenson W.H. and Brown P.E. The production of artificial manures. Agr.
1930   Exp. Sta. Res. Bull. 126.

Söchtig H. Untersuchungen über die Wechselwirkung zwischen Tonmineralen und hetero-
1957   polaren organischen Linearkolloiden. Dissertation der Hohen Landwirtschaft-
            lichen Fakultät der Christian Albrechts-Universität, Kiel. p. 125 + 12.

Söchtig H.   Beeinflussung des Stoffwechsels der Pflanzen durch Humus und seine
1964   Bestandteile und die Auswirkung auf Wachstum und Ertrag. Landbauforsch.
            Völkenrode 14:9-16.

Söchtig H.   Uber den Einfuss von N-Lignin auf die Nitrifizier·n   im Boden sowie den
1970   Ertrag und den Nitratgehalt der Pflanzen. Qual. Plant. Mater. Veg. 20:137-150.

Söchtig H.   Vorkommen von chemischen Verbindungen in Torfstoffen und Anderungen ihrer
1974   Konzentration unter verschiedenen Bedingungen. Telma 4:255-270.

Söchtig H. and Flaig W. Herstellung und Wirkung eines organischen Stickstoffdüngers
1974   aus den Sulfitablaugen der Zellstoffindustrie. Landw. Forschung 30 (11).
            Sonderh:17-24.

Söchtig H. and Harms H. Uber den Einfluss von Torf auf Keimung und Anfangswachstum
1971   von Pflanzen. Landw. Forsch. 26 (11). Sonderh:168-174.

Söchtig H. and Maciak F. Bindung des Stickstoffs und Vorkommen phenolischer Verbin-
1971   dungen im Torf. Telma 1:49-61.

Söchtig H., Harms H. and Haider K. Uptake and transformation of ^{14}C-labelled phenolic
1968   acids by wheat seedlings. In: Isotopes and Radiation in Soil Organic Matter
            Studies. IAEA, Vienna. p. 531-540.

Some aspects of green manuring. Soils and Fertilizers 12:155-159.
1949

Sørensen H.   Studies on the decomposition of ^{14}C-labelled barley straw in soil. Soil
1963   Sci. 95:45-51.

Sørensen H.   Formation of soil organic matter during decomposition of plant components.
1966   In: The Use of Isotopes in Soil Organic Matter Studies. Report of the FAO/
            IAEA Tech. Meeting. Pergamon, Oxford. p. 271-274.

Springer U. and Lehner A. Stoffabbau und Humusaufbau bei der aeroben und anaeroben
1952a   Zersetzung landwirtschaftlich und forstwirtschaftlich wichtiger organischer
            Stoffe. I. Z. Pflanzenernähr., Düng., Bodenkunde 58:193-231.

Springer U. and Lehner A. Stoffabbau und Humusaufbau bei der aeroben und anaeroben
1952b   Zersetzung landwirtschaftlich und forstwirtschaftlich wichtiger organischer
            Stoffe. 11. Z. Pflanzenernähr., Düng., Bodenkunde 59:1-27.

Staudinger H. Organische Kolloidchemie, 2. Aufl. Braunschweig, Verlag Vieweg.
1941

Stevens R.M. Green land - clean streams. Temple University, Philadelphia, Pa.
1972

Stewart J. and Leonhard C.D. Use of chelates in citrus production in Florida. Soil Sci.
1957   84:87-97.

Stewart B.A., Johnson D.D. and Porter L.K. The availability of fertilizer nitrogen
1963   immobilized during decomposition of straw. Soil Sci. Soc. Amer. Proc. 27:
            656-659.

Stöckli A. Uber den Abbau von Lignin, Cellulose und Hemicellulose durch Pilze. Versuche
1952   mit Streumaterialien, Holz und Ligninsulfonsäure. Promotion ETH Zürich.

Struthers P.H. and Sieling D.H. Effect of organic anions in phosphate precipitation by
1950   iron and aluminium as influenced by pH. Soil Sci. 69:205-213.

Süss A. and Wagner A. Die Sorption von Herbiziden an verschiedenen Bodenkomponenten.
1969   Z. Pfl. Krankh. Pfl. Path. Pfl. Schutz 76:529-536.

Sullivan J.D. and Felbeck G.T. A study of the interaction of s-triazine herbicides with
1968   humic acids from three different soils. Soil Sci. 106:42-52.

Swenson R.M., Cole C.V. and Sieling D.H. Fixation of phosphate by iron and aluminium
1949   and replacement by organic and inorganic ions. Soil Sci. 67:3-22.

Theng B.K.G. The Chemistry of Clay-Organic Reactions. Adam Hilger, London. 343 p.
1974

Thornton J.I., Crim D. and McLaren A.D. Enzymatic characterization of soil evidence.
1975   J. Forensic Sciences 20:674-692.

Tietjen C. Plant response to manure nutrients and processing of organic wastes. Proc.
1966   N ation. Symp. Management of Farm Animal Wastes. Amer. Soc. Agric. Eng.,
            St. Joseph, Michigan.

Tietjen C. European experiences in applying sludge to farmland. Compost Science, 4-6
1973   July 1973, Emmaus, Pennsylvania.

Tietjen C. Influence of antibiotics and growth promoting feed additives on the manuring
1975a   effect of animal excrements. Proc. 3rd Int. Symp. Livestock Wastes. Amer.
            Soc. Agric. Eng., St. Joseph, Michigan.

Tietjen C. The agricultural reuse of municipal wastewater in Braunschwieg, Germany.
1975b   Confernece on Wastewater Renovation and Reuse at the Rockefeller Foundation
            Center in Bellagio, Italy, 16-21 July 1975.

Tischler W. Synökolgie der Landtiere. Gustav Fischer-Verlag, Stuttgart, 414 S.
1955

Tolpa S. Stimulators and inhibitors isolated from peat and possibilities of their application
1972   in plant production and animal feeding as well as in animal and human therapeutics.
            Proc. 4th Int. Peat Congr., Otaniemi, Finland 4:31-36.

Trojanowski J. Przemiany substancji organicznych wglebie. Państwowe Wydawnictwo
1973   Rolnicze i Leśne, Warszawa. (Polish). 331 p.

Tyurin I.V. Soil organic matter and its role in soil formation and soil fertility. Sel
1975   Khozgiz (1937), Cit. Kononova 1975.

Umweltbundesamt Verwertung von Klärschlämmen im Landbau. Merkblatt 7. Hdb. Müll-
1972   und Abfallbeseitigung, 6854. Schmidt Verlag, Berlin.

Valla A., Guckert A. and Jacquin F. Formation de complexes entre acides humiques et
1972 a   montmorillonite. I. Etude des mécanismes d'adsorption d'acides humiques -
            ^{14}C en fonction des cation. Bulletin de l'ENSAIA de Nancy, XIV:227-238.

Valla A., Guckert A. and Jacquin F. Formation de complexes entre acides humiques et
1972b   montmorillonite. II. Etude de la stabilité des complexes acides humiques -
            ^{14}C-montmorillonite à l'égard des réactifs d'extraction chimiques. Bulletin
            de l'ENSAIA de Nancy, XIV:239-244.

Vam (N.V. Vuilafvoer Maatschapij) Mededelingen 1960, 1964, 1968, 1972. Amsterdam.

Verma L., Martin J.P. and Haider K. Decomposition of carbon-14-labelled proteins,
1975   peptides and amino acids: free and complexed with humic polymers. Soil Sci.
            Soc. Amer. Proc. 39:279-284.

Virtanen A.I. Om växterna förmaga att upptage jordens organiska bestandsdelar. Nordisk
1935   Jordbrugforskning. 17:203.

Virtanen A.I. and Linkola H. Organic nitrogen compounds as nitrogen nutrition for higher
1946   plants. Nature 158:515.

Voets J.P. and Dedeken M. Soil enzymes. Mededelingen Rijksfaculteit Landbouwweten-
1966   schapen, Gent 31:177-190.

Voorhoeve van J.J.C. Organic fertilizer problems and potential for developing countries.
1974   World Bank Fertilizer Study, Background Paper 4, I.F.C. Office of the
     Economic Adviser, Washington.

Waksman S.A. and Smith J.W. Transformation of methoxyl group in lignin in the process
1934   of decomposition of organic residues by microorganisms. J. Amer. Chem. Soc.
     56:1225.

Waksman S.A., Tenny F.C. and Diehm R.A. The chemical and microbiological principles
1929   underlaying the transformation of organic matter in the preparation of artificial
     manures. JASA 21:533-545.

Walker S.A. and Crawford D.V. The role of organic matter in adsorption of the triazine
1968   herbicides by soils. In: Isotopes and Radiation in Soil Organic Matter Studies.
     IAEA, Vienna. p. 91-105.

Wallace A., Müller R.T., Lunt O.R., Ashcroft R.T. and Shannon L.M. Comparisons of
1955   five chelating agents in soils; in nutrient solutions, and in plant responses.
     Soil Sci. 80:101-108.

Weed S.B. and Weber J.B. Pesticide-organic matter interactions. In: Pesticides in
1974   Soil and Water. W.D. Guenzi (Ed). Soil Sci. Soc. Amer., Madison, Wisconsin.
     p. 39-66.

Whitehead D.C. Identification of p-hydroxybenzoic, vanillic, p-cumaric and ferulic acids
1964   in soils. Nature 202:417-418.

Williams E.G. Some aspects of phosphate retention and availability in soils. Trans. 7th
1960   Int. Congr. of Soil Sci. 3:602-611.

Winter A.G., Brüsewitz G. and Schönbeck F. Untersuchungen über die Aufnahme
1960   organischer Substanzen durch die Wurzeln höherer Pflanzen. VI. Die Bildung
     allochthoner Substanzen in Weizen auf natürlichen Böden. Naturwiss. 47:139-140.

Winter A.G., Preuss H. and Schönbeck F. Untersuchungen über die Aufnahme organischer
1959   Substanzen durch die Wurzeln höherer Pflanzen. I. Phenolische Verbindungen.
     Naturwiss. 46:537.

Winter A.G. and Schönbeck F. Untersuchungen über die Aufnahme organischer Substanzen
1959   durch die Wurzeln höherer Pflanzen. II. Phenolische Verbindungen. Naturwiss.
     46:536.

Woodruff C.M. Estimating the nitrogen delivery of soil from the organic matter deter-
1949   mination as reflected by Sanborn Field. Soil Sci. Soc. Amer. Proc. 14:208-212.

Yoshida T. and Ancajas Rosabel R. Nitrogen-fixing activity in upland and flooded rice
1973   fields. Soil Sci. Soc. Amer. Proc. 37:42-46.

Zohar Y. Amelioration of desert soil by peat amendment. Syp. Comn. III. Intern. Peat
1975   Soc. June 1975, Israel.