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THE BIOCHEMISTRY OF SOIL HUMUS - SOME CURRENT CONCEPTS

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The biochemistry of soil organic matter (SOM) is discussed with special attention to the characterization of soil humus. A clear picture of the composition of SOM is obtained from the flow-sheet diagram which fractionates SOM into its component groups.

The formation of humic substances is examined and the sequential steps in its synthesis presented schematically. The structural chemistry of the humic acids is briefly discussed and a molecular arrangement in harmony with the requirements presented.

INTRODUCTION

Over the past few years there has been an increasing interest regarding the use of soil organic matter in improving soil conditions in tea estates.

An understanding of the nature of soil organic matter (SOM) may therefore provide a more rational basis for its effective use—which is the objective of this paper. But in the space of this communication, it is not possible to cover all aspects of SOM, and therefore this paper will be confined to the biochemistry of soil humus.

Components of soil organic matter

The nature of soil humic substances has been the subject of scientific investigations over a long period of time. However, there still appears to be a lack of unanimity in the precise definition of the term ' humus '. This is understandable because soil humus is the product of the interaction of many biotic, physical and chemical soil environmental factors over time. To clarify the position therefore, it would be pertinent to examine the components of soil organic matter.

Figure 1 provides a commonly accepted scheme of fractionation of the different soil organic components.

Using this scheme we could re-group the organic components to arrive at the following definitions.

1. S.O.M. = Humus + Biomass + Mulch
2. Humus = Humic matter + non-humic matter.
3. Humic matter = Humic acid + Fulvic acid + Humins
4. Non-humic matter = soil polysaccharides + ' free ' low molecular weight components

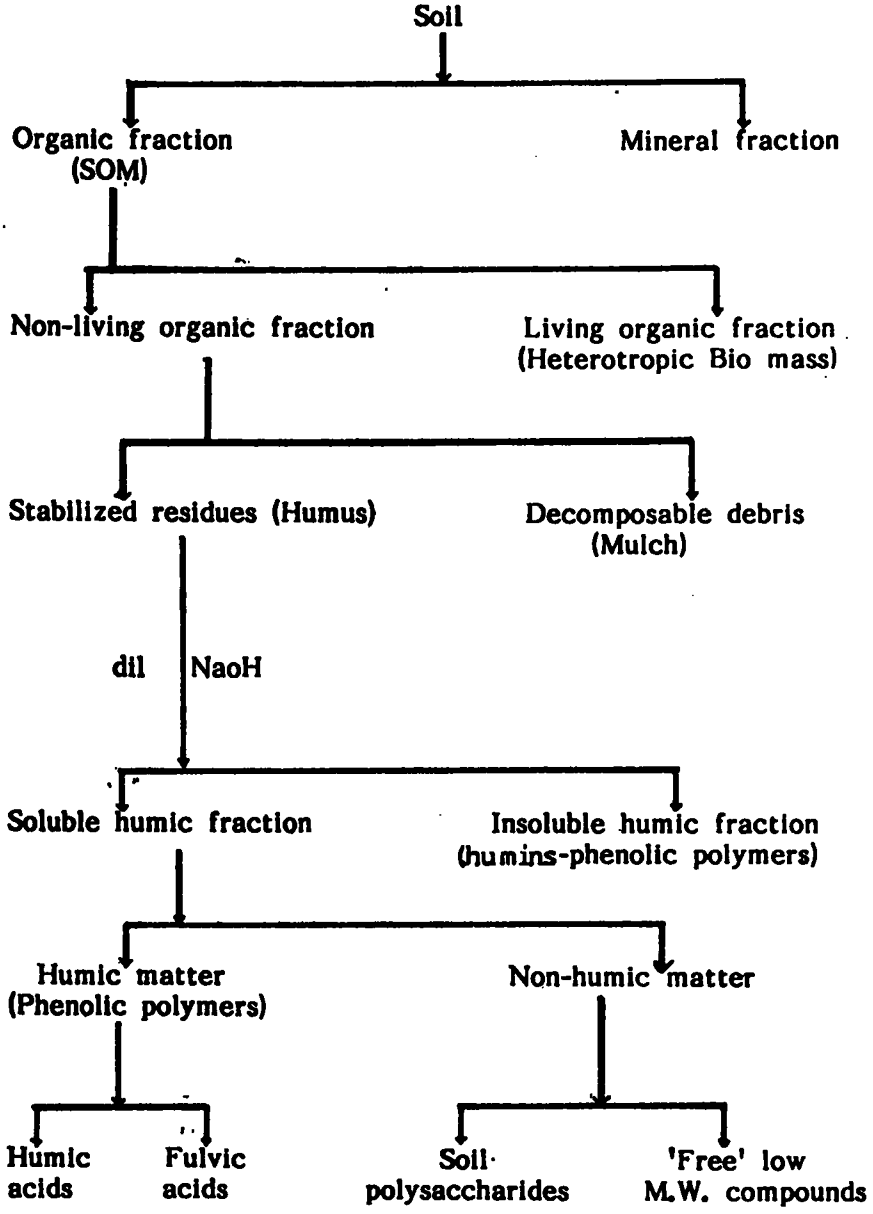

Fig. 1.– Organic components of soil.

Jansson (1966) conceives soil organic matter as an ecological system comprising of three biological fractions, *viz.* the decomposable debris, the living heterotropic biomass, and the stabilized humus (Fig. 2).

Soil organic matter would therefore consist of a series of products ranging from undecayed plant and animal tissues through ephemeral products of decomposition of fairly stable amorphous brown to black material having no trace to the anatomical structure of the material from which it was derived, and referred to by the generic term humus. Humus would comprise the products of mineralization and humification in various stages of transformation, and would therefore be expected to be a heterogenous fraction.

Components of Humus

This fraction may be broadly divided into humic and non-humic substances. The latter include those whose physical and chemical characteristics are still recognizable such as carboydrates, proteins, amino acids, organic acids and other low molecular substances. By contrast, humic substances no longer exhibit specific physical and chemical characteristics (such as sharp melting point, exact refractive index, etc) normally associated with well-defined organic compounds. Humic substances are dark-coloured, acidic, predominantly aromatic, chemically complex materials that range in molecular weights from a few hundred to several thousand. Humic compounds are also negetively charged colloids.

The humic materials are usually partitioned into the following three main fractions, *viz* :

(*a*) humic acid (HA), which is soluble in dilute alkali, but precipitated on acidification of the alkaline extract to (*b*) fulvic acid (FA), which is soluble in dilute alkali as well as acid, and (*c*) humin which is that humic fraction that cannot be extracted from the soil by dilute base or acid.

From published analytical data structurally the three humic fractions are similar, but differ in molecular weight, ultimate analysis and functional group content. The chemical structure and properties of the humin fraction appear similar to those of HA. The insolubility of humin seems to arise from it being firmly adsorbed on or bonded to inorganic soil constituents (Schintzer, 1978).

It might appear from the above scheme that there are clear-cut differences between non-humic and humic fractions of soil organic matter and among the other classes of humic substances. Unfortunately this does not appear to be the case, since these fractions are largely defined on an operational basis. There is no sharp line of demarcation and both types of substances are present at all times in many soils and there is a constant change of the former into the latter even if slowly.

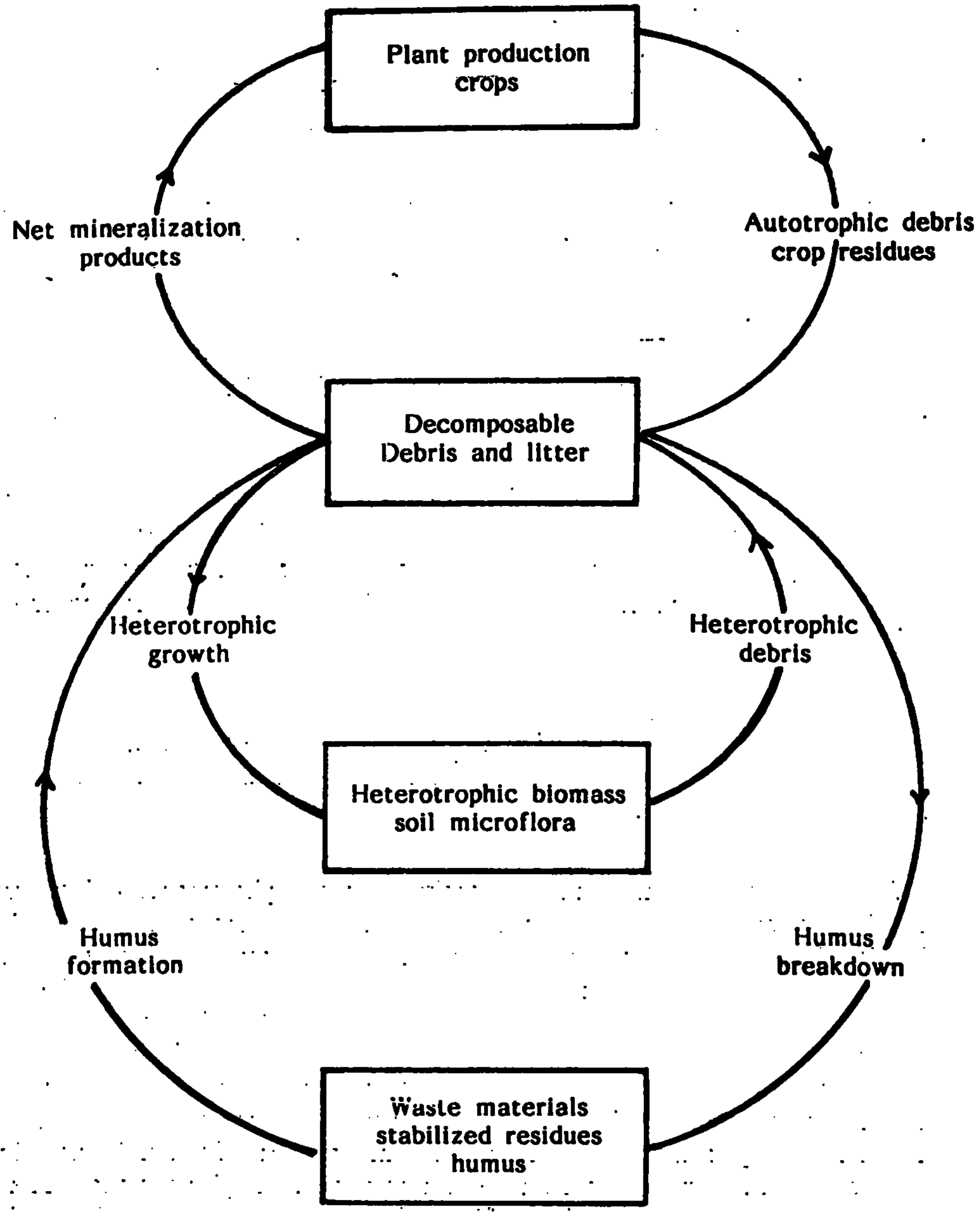

Fig. 2. — Schematic illustration of ecological organic-matter transformations taking place in soil.

Formation of humic substances

Chemical degradation studies indicate that humic compounds are complex polymers of phenolic units. Because lignins are phenolic polymers and major plant constituents which are relatively resistant to microbial decomposition, they are generally considered to be a major, if not the primary source of phenolic units for humic acid synthesis (Flaig, Beutelspacher and Rietz, 1975). Numerous organisms are able to slowly decompose lignin or its partial decomposition products.

Phenolic units for synthesis of humic compounds may also originate through microbial synthesis from non-aromatic carbon and energy sources. Numerous phenolic and hydroxy benzoic acid compounds are synthesized by fungi and other microorganisms.

Figure 3, represents the present day concepts of the formation of humic substances (Martin and Haider, 1971). The major sequential steps of this scheme are ;

(*a*) Phenolic units may be formed through microbial degradation of lignin and other plant polyphenols or through synthesis by soil microorganisms, (*b*) these units undergo enzymatic or auto-oxidative reactions to form highly active radicals which link with other phenolic units, peptides and amino acids to form large humic acid molecules.

Structural chemistry of humic substances

It would suffice to dwell on the outstanding work done by Schintzer (1977) and co-workers over the last decade in advancing our knowledge of the structural chemistry of humic materials.

Schintzer and his team from their analytical, spectrophotometric and spectrometric data, and the information provided by chemical degradation, showed that humic substances formed under widely differing climatic conditions had essentially similar chemical structures and characteristics. Major humic 'building blocks' were in all instances complex phenolic and benzene-carboxylic structures. Data from physico-chemical studies showed that humic and fulvic acids behave like linear, flexible polyelectrolytes that are readily aggregated most likely with the aid of H-bonding at low pH, but dispersed because of increased dissociation of functional groups at higher pH. Thus at becomes apparent that humic and fulvic acids are not single molecules but molecular associations of phenolic and benzene-carboxylic compounds ("building blocks") of microbiological, polyphenolic, lignin and condensed lignin origins. The 'building blocks' appear to be held together by weak linkages, mainly H-bonds.

A chemical structure (Fig. 4) that is in harmony with most of the requirements listed above has been proposed by Schnitzer (1977).

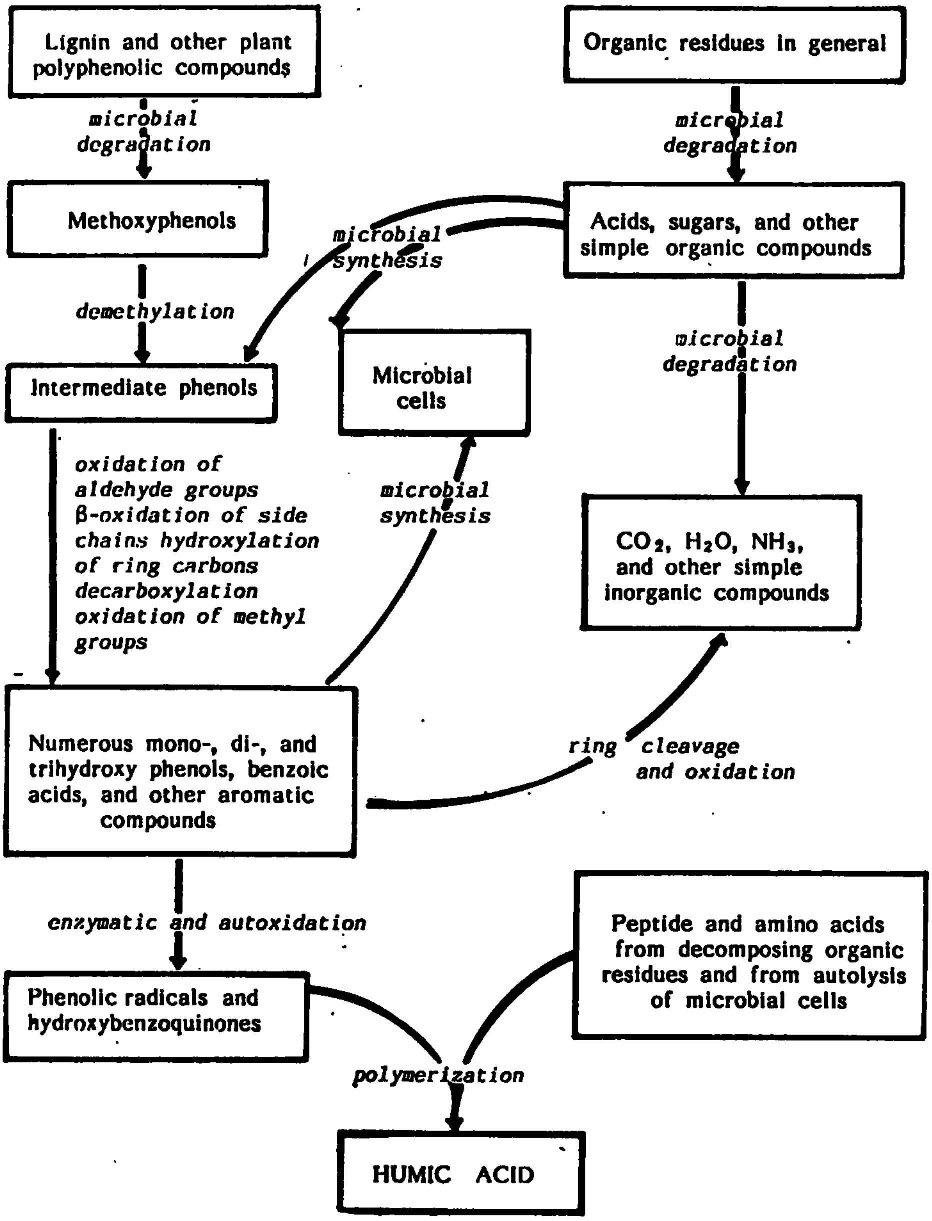

Fig. 3. – A schematic representation of humic acid synthesis in soil.

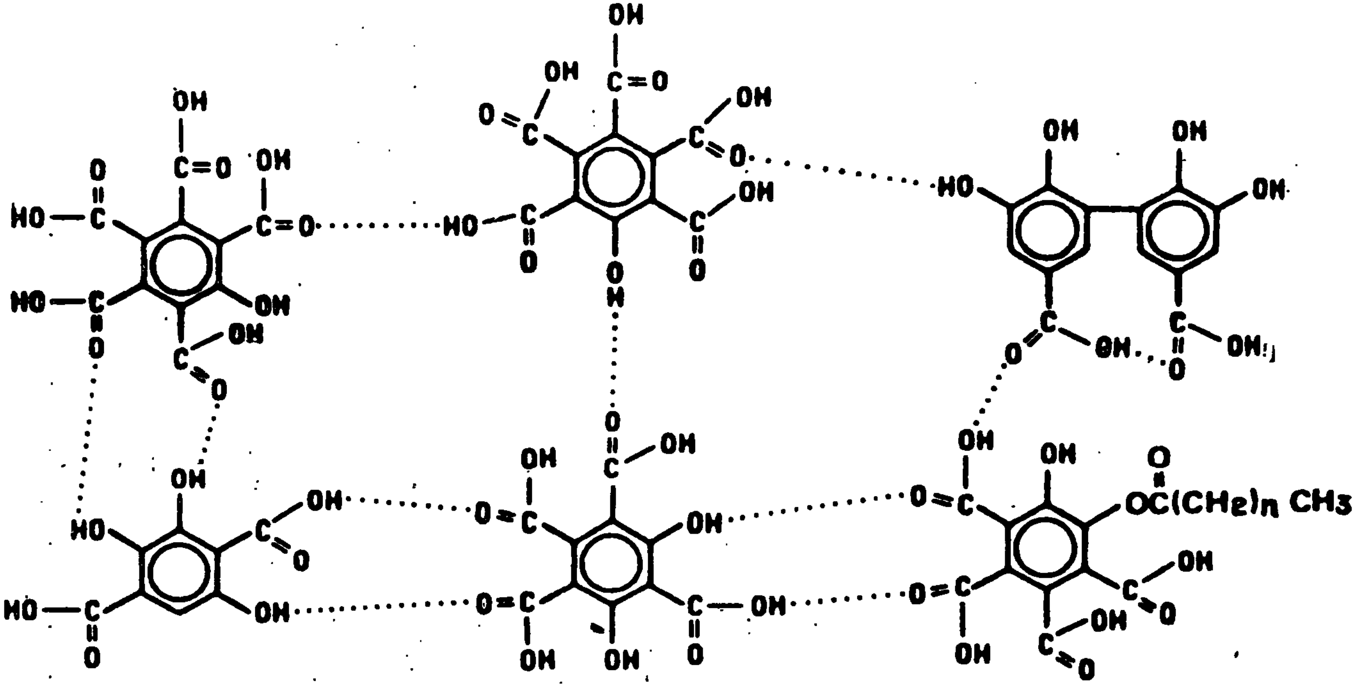

Fig. 4. — Partial structure of Fulvic acid.

Characterization of humic materials

Chemical investigations have shown that while the basic structural unit of humic compounds are phenolic, peripheral parts of the molecule contain functional groups. The major oxygen - containing functional groups are carboxyls, phenolic hydroxyls and carbonyls. The total acidity equals the sum of carboxyl and phenolic hydroxyl groups although the contribution by the carboxyl group predominates. Further the total acidity and carboxyl acidity of the FAs were in all instances considerably higher than those of HAs.

Some of the important physico-chemical properties of humic substances are related to these active functional groups.

(1) Cation-exchange capacity

The cation-exchange capacity (CEC) of the organic fraction of soils is primarily due to the occurrence of exchangeable hydrogens in the carboxyl and phenolic hydroxyl groups of humic compounds.

Ionization of these functional groups is pH-dependant. The carboxyl groups ionize in the acid scale while the phenolic hydroxyl group ionize at pH 6. Since the CEC of humus arises from the dissociation of these groups, this value of CEC increases at higher pH.

The exchange capacity of humus is appreciably higher than that of clays, being of the order of 200-300 m.eq. per 100 g dry matter. This has the consequence that the CEC of soils low in clay, or only containing clays with a very low exchange capacity in the acid or sub-acid range is very dependant on their humus content.

(2) Buffer capacity

As stated earlier, the ionization of the functional groups is pH dependant, and this confers on the humic material, buffering properties, e.g. when the acidity of the soil tends to increase say due to ammonium sulphate fertilization, the dissociation of the carboxyls and hydroxyls can be retracted and *vice-versa.*

The buffering capacity of a soil is of great practical importance. If it did not exist, it would be difficult to conceive of agriculture as we know it today. Both acids and bases are produced more or less continuously in field soils and if there was no buffer present marked fluctuations in pH would follow killing or injuring many plants. Since most crops grow well only where the pH remains within a fairly narrow controlled range, the more the humus the better is the soil buffered.

(3) Chelation of metals

Carboxyl and phenyl hydroxyl groups have been implicated in organometallic reactions of humic matter with metals. A simple illustration is provided in Fig. 5.

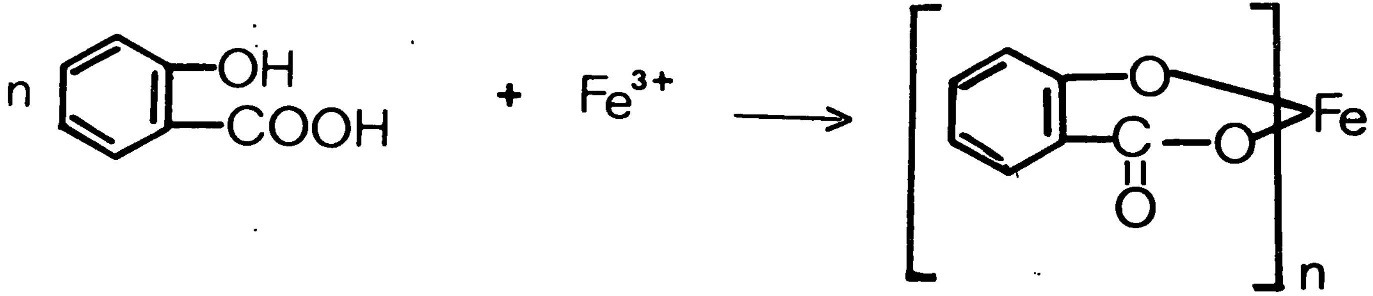

Fig. 5. – Organo – metallic reactions of humic matter.

The supply of trace elements to plants is frequently limited not by the total quantities in soil, but by precipitation of insoluble forms, the best known example being the low availability of iron and manganese in calcareous soils. Such deficiencies can often be overcome by application of synthetic metal chelates, the plant being able to liberate the metallic cation, either at the root surface or after absorption of the whole chelate. In view of this ability of plants to utilize the cations from synthetic chelate molecules, it is expected that naturally occurring chelates would influence the availability of metal trace elements. It is well established that humic matter forms stable complexes with polyvalent metal cations (Khanna and Stevenson, 1962) and this may be one of its most important property and function in soil.

The major source of soil acidity in strongly acidic soils is the dissolution and hydrolysis of Al to release H ions. Therefore could the ability of humic materials to form chelates or complexes with metal ions like Al be helpful in the amelioration of high acidity? Hoyt and Turner (1975) found beneficial effects of addition of large quantities of organic materials to very acid soils i.e. reducing exchangeable Al and increasing pH. These effects were attributed to complexing of Al by components of the organic material. However these beneficial effects were temporary because within six months all these parameters returned to the original values. Thus it appears that the addition of large quantities of organic materials cannot be considered a satisfactory substitute to liming of very acid soils.

Water-retention

Humus exhibits properties of a typical hydrophyllic colloid. It can absorb large amounts of water, and increase the water-holding capacity of the soil. Absorption capacity of humus is about five-fold that of clay. But the same hydrophyllic property makes the humic matter hold the water rather tightly so that ' available water ' to the plants could be limited. But this could be of benefical importance to the microbial life during a drought.

Non-humic matter

Soil polysaccharides or " Microbial Gums "

The major polymeric material in the non-humic fraction of humus are the soil polysaccharides, which have been commonly referred to as " microbial gum."

Investigators have given far less attention to soil polysaccharides than to humic substances. The polysaccharide fraction is the second most important component of humus and may account for 10 to 30 per cent of the total and is probably of great importance with respect to soil aggregation or binding.

Polysaccharides are common constituents or metabolic products of all forms of living organisms. The constituent units of the soil polysaccharides could originate from plant and animal residues and from microbial synthesis in soil. Because most plant and animal polysaccharides are subjected to microbial degradation or because of the complexity of the soil polysaccharide fraction, it has been assumed that the microbial polysaccharides may be the most important source of this soil fraction. Most plant and microbial polysaccharides contain one to three and rarely four or five different monomer units. The soil polysaccharides on the other hand contain ten or more different major units and many others in different concentrations. According to Martin and Haider (1971) who have worked extensively in this field the soil polysaccharides fraction could be built up in a manner having certain similarities to the humic fraction. Plant and microbial polysaccharide units in all stages of degradation could serve as constituent units for the formation of new polymers peculiar to the soil environment. Extra cellular enzymes or enzymes released during autolysis of the microbial bodies could link the units. Combinations which are relatively resistant to degradation or which become resistant through salt or complex formation with metal ions and/or clays would constitute the polysaccharide fraction of the soil.

Significance to soil structure

The presence in the soil of gum-like polysaccharides which are capable of bringing about aggregation has been demonstrated by many workers. Further, there are a number of studies which show good correlations between 'microbial gum' and aggregation. In general, present evidence leads to the conclusion that polysaccharides make a significant contribution to aggregate stability in some soils, particularly cultivated soils of relatively low organic matter (Lowe, 1978).

Effectiveness of various kinds of organic matter in soil aggregation

It is often said that there is a close correlation between the organic matter in soils and the degree of aggregation and tilth. This is generally true, but not all kinds of OM act as effective stabilizing agents. Materials such as peat and sawdust and essentially all kinds of undecomposed crop residues have little effect in the stabilizing of aggregates, although they do help keep aggregates small. As OM sources undergo decomposition, microbial slimes are produced that do have marked stabilizing properties as mentioned earlier. The quantity produced per unit time is usually directly related to the amount of crop residues present and their rate of decomposition. These microbial gums are known to consist largely of polysaccharides, polyuronides, cellulose and humus breakdown products and their linear organic polymers.

Since it is primarily the products of microorganisms that are the stabilizers it is obvious that even well rotted manures and composts are not especially active as stabilizing agents. Their immediate effects are largely dependant upon their content of microbial slimes and related materials at the time they are used. If they contain considerable available energy source, as they undergo further decomposition, microbial gums will be synthesized which will have the usual favourable effect on a aggregation if they contact the aggregates and act as cements before they themselves undergo decomposition. Manure that has been stored under anaerobic conditions for example is obviously not thoroughly decomposed and when exposed to the air, the aerobic flora can synthesize abundant supplies of polysaccharides.

Root residues are superior to top residues in providing good soil aggregation, because roots are well distributed through the soil, thus the gums and polysaccharides arising from their decomposition are also well distributed and in a position to act as cement between soil particles as they are being formed into aggregates by the pressure of the roots. This type of fixation tends to protect the gums from decomposition by microbes. Top residues are also sources of gums but they are not intimately mixed with soil, thus the gums produced are rapidly decomposed and do not move far from the soil surface. The above facts are in keeping with the observation that after a period of years under grass a soil will normally have a higher content of organic matter and a higher degree of aggregate stability than a similar soil after a period of years under arable cropping.

The underlines the importance of root residues in the rehabilitation of tea lands with Guatemala or Mana grass. On this score, the grass variety which produces a more copious root system is to be preferred for rehabilitation.

The effectiveness of different kinds of OM in aggregation apply to OM that is incorporated with the soil. Most OM that is used as a long term mulch will improve aggregation and structure, but this may be largely through prevention of raindrop splash, improved moisture conditions, higher earthworm populations and lack of mechanical disturbance (Allison, 1973).

It is common to restrict discussion of SOM problems to the non-living matter and particularly the humic fractions. However, since the living and dead fractions of SOM are so intimately bound together with regard to their formation and functions, this restriction cannot be maintained in discussion on soil improvement.

According to Jansson (1966) the general situation with regard to soil organic matter research may be characterised in the following way. On the one hand we have humus chemistry concentrating on the humic substances, on certain fractions of the dead organic material of the soil while on the other hand we have soil microbiology, concentrating on the living organic material in the soil, the organisms constituting it, their activities and their supply of energy and nutrient elements. Between humus chemistry on the one hand and soil microbiology on the other we have the relationships of soil fertility to soil organic matter. These relationships include the active and passive functions of SOM. The active functions are connected with the living organic fraction and include energy transformations leading to net mineralisation of plant nutrients, soil aggregation and structure stabilisation. The passive functions depend particularly on the presence of the dead organic fraction. They affect the physical and colloid-chemical properties of the soil, increase the ion-exchange capacity and make possible the formation of organo-mineral complexes.

In conclusion, it may be said that the substance of the above discussion is truthfully reflected in the legend

" Humus – the Soul of the Soil "

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