

Organic Matter and Soil Fertility

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Paper presented at the 1993 Obihiro Asia and the Pacific Seminar on Education for Rural Development held at Obihiro University of Agriculture and Veterinary Medicine, Obihiro, Hokkaido, Japan on Sep. 5-15, 1993

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1. Introduction

Organic matter is very important for maintaining the fertility of arable soils. This has been well recognized since mankind started agricultural practice. In fertile soils plants grow well, and large amounts of plant material are produced and returned to the soil. As a consequence, fertile soil always accumulates a moderate amount of organic matter. In subsistence agriculture, mankind imitated this natural process of self-fertilization.

In modern intensive agriculture, the importance of organic matter is apt to be forgotten. This is because mankind found that organic matter is not an essential nutrient of plants and he can grow plants more efficiently by supplying only the mineral nutrients. Under such circumstances, however, various soil related problems such as deterioration of arable land and occurrence of crop diseases have been recognized. The safety of food is also threatened from the overuse of pesticides.

We have to reanalyze the role of soil organic matter in plant production. For this analysis, more thorough and scientific knowledge of soil organic matter is necessary.

Table 1. Global carbon reservoirs
(after Eswan, H. Berg, V. D. and Reich, P 1993)

Reservoirs	Carbon (Gt)
Land	
Plant	550
Soil	1500
Atmosphere	750
Ocean	38000
Fossil Fuel	4000
Crust of Earth	65.5 x 10 ⁶

1Gt = 10⁹t

2. The amount of soil organic matter (SOM) on earth

The carbon on land is composed of ca. 550 giga tones (Gt) of plant biomass C and 1,500 Gt of SOM C (Paul and Clark, 1988). The amount of SOM carbon is thus three times as large as plant biomass C and two times as large as atmospheric C (Table 1). In the pre-historical age, however, soil organic carbon was estimated to attain even 2,014 Gt (Buringh, 1984). The civilization and agricultural practice of mankind has greatly influenced the balance in the carbon reservoir by the exhaustion of SOM. This is as significant as the well known effect of

the combustion of fossil fuels. Global warming caused by these human activities accelerates the release of carbon dioxide from the SOM pool by increasing its decomposition (Jenkinson, 1991). This leads to the never ending feed back effect that promotes global warming. Soil organic matter occupies the largest pool in the cycling of organic matter in the land ecosystem. Its change has therefore a serious effect.

3. Composition of soil organic matter(SOM)

Soil animals and microbes occupy less than 5% of the organic matter existing in soils. The rest of it (95%) is composed of dead organic matter under decomposition or re-synthesis into humic substances (Fig. 1). Though they have no life, these organic matter are changing dynamically under the action of soil biota and support the life on the earth.

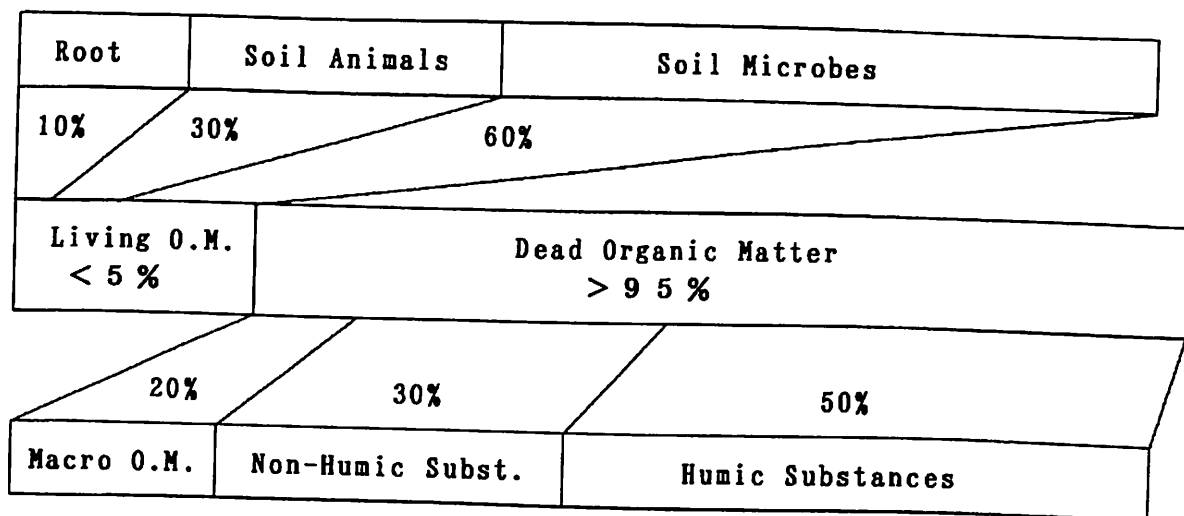


Fig. 1. Composition of soil organic matter

SOM may be grouped into macro debris, non humic substances, and humic substances.

Macro debris constitute ca. 20% of SOM. They are mainly composed of the litter of plants in which the original texture is still recognizable. It is also called a light fraction after being seperated by a heavy solution.

Non-humic substances occupy ca. 30% of SOM. They are substances released into soils from living things, e.g. proteins, enzymes, polysaccharides, and lipids. They can be purified and their structure is identifiable by chemical methods.

Humic substances occupy ca. 50% of SOM. They are formed from macro debris and non-humic substances in soils. They are amorphous, dark colored, and are high molecular weight organic compounds specific to soil.

However, it is actually difficult to separate these groups. It is practical to consider that these three groups are under continuous transformation for the following reasons:

- (1) Formation of humic substances is begun in the macro debris.
- (2) A large part of non-humic substances which correspond to the known class of compounds, such as polysaccharides, proteins, and lipids, are altered considerably.
- (3) A considerable portion of non-humic substances are bound to humic substances by covalent bonds, ionic forces, and van der Waals forces. Relative composition of macro debris, non humic substances, and humic substances differs also by types, conditions, and profiles of soils.

There is also an idea to classify soil organic matter into the following five fractions (Jenkinson and Rayner, 1977):

- (1) Decomposable plant material,
- (2) Resistant plant material,
- (3) Soil microbial biomass,
- (4) Physically stabilized fraction of SOM,
- (5) Chemically stabilized fraction of SOM.

In this model (Fig. 2), physically stabilized fraction means the organic matter protected from decomposition in soil aggregates, while chemically stabilized fraction means the humic substance which acquired very high stability in the process of humification. Whether these fractions exist actually or independently has not been demonstrated as yet, however.

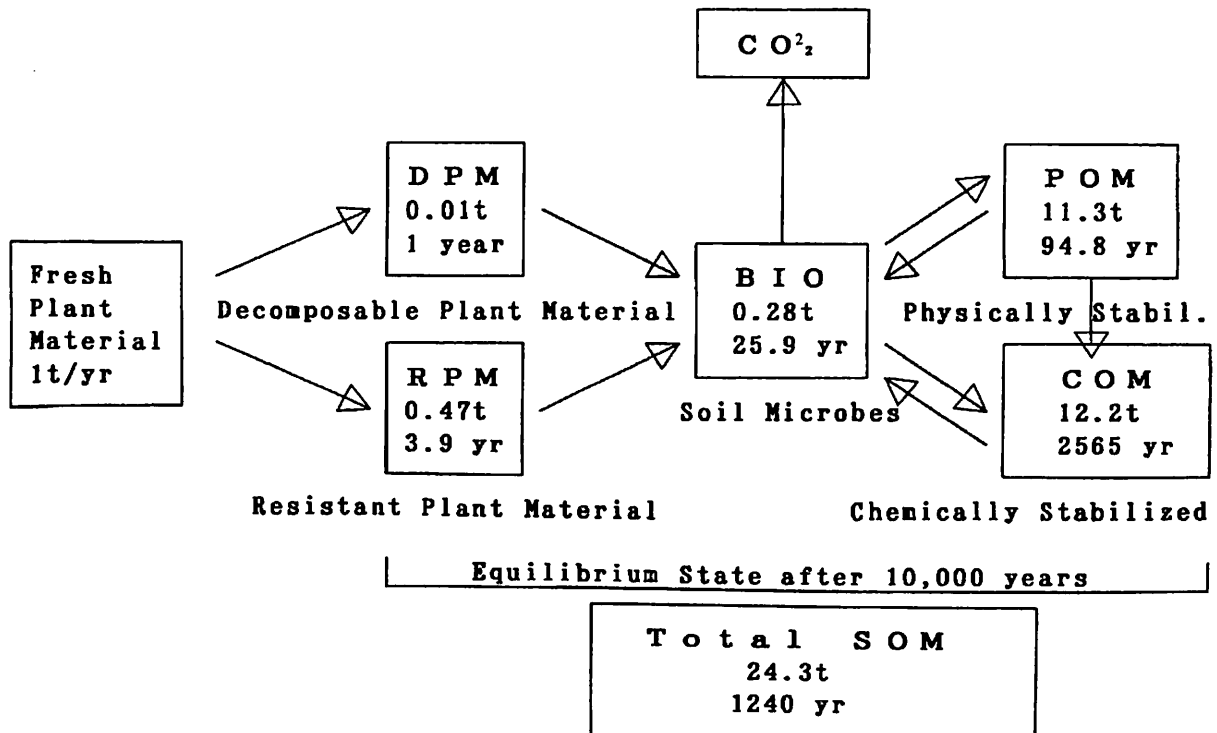


Fig. 2. Dynamics of soil organic carbon (Jenkinson and Rayner, 1977)

4. Extraction and separation of soil organic matter into fractions.

4-1. Extraction

Humic substances have a large amount of dissociative or hydrophilic groups such as carboxyl, phenolic hydroxyl, and alcoholic hydroxyl group. In spite of this, humic substances are largely insoluble in water, because these dissociative groups are bound with proton and polyvalent cationic metals, such as aluminum, calcium, magnesium, and iron, which suppress the electrostatic repulsion of humic polymers. Under such conditions, humic substances are adsorbed by clay minerals, or coagulate each other due to the hydrophobic interaction of aliphatic and aromatic moieties.

Diluted sodium hydroxide solution replaces the proton with Na ion and transforms Al ion to aluminate ion and displaces it from the dissociative groups. This promotes the dissolution of humic substances. The efficiency of sodium hydroxide in the extraction of humic substances is low in soils saturated with calcium and magnesium, however. Sodium pyrophosphate extracts humic substances from such soils by its chelate forming ability. Washing the soil with acids before the extraction with alkali also increases the yields in these soils.

The hydrophobic property of humic substances also facilitates the extraction of humic substances. Aprotic polar organic solvents (e.g. dimethylsulfoxide, dimethylformamide) are good extractants for humic substances. Acidified dimethylsulfoxide is often as effective as sodium hydroxide as an extractant of humic substances (Hayes, 1991).

4-2. Fractionation

Soil organic matter extracted by various methods are separated into two fractions, i.e. the humic acid fraction which precipitates at pH 1.0 by adding HCl or H₂SO₄ and the fulvic acid fraction which remains in solution even at pH 1.0. To purify the fulvic acid fraction, methods such as dialysis, gel-filtration, and ultrafiltration are used. Loss of low molecular weight constituents in fulvic acid is thereby inevitable (Fig. 3).

The fulvic acid fraction is also treated with XAD8 (a macro-reticular resin), Duolite-A7 (a weak basic ion exchanger), or Polyclar-AT (a polyvinyl pyrrolidone resin polymer) under acidic condition. The component of fulvic acid fraction rich in humic substances is adsorbed on these resins, while the component rich in polysaccharides passes through the column of resin (Thurman and Malcolm, 1981; Malcolm, 1991).

The humin fraction denotes the soil organic matter which can not be extracted from soil by alkali or chelating agents. A part of humin fraction can be solubilized by extraction with dimethyl sulfoxide or by destroying the mineral constituents with hydrogen fluoride. Once separated from soil, or by treating it with a chelating agent, it becomes largely soluble in alkali (Tsutsuki and Kuwatsuka, 1992).

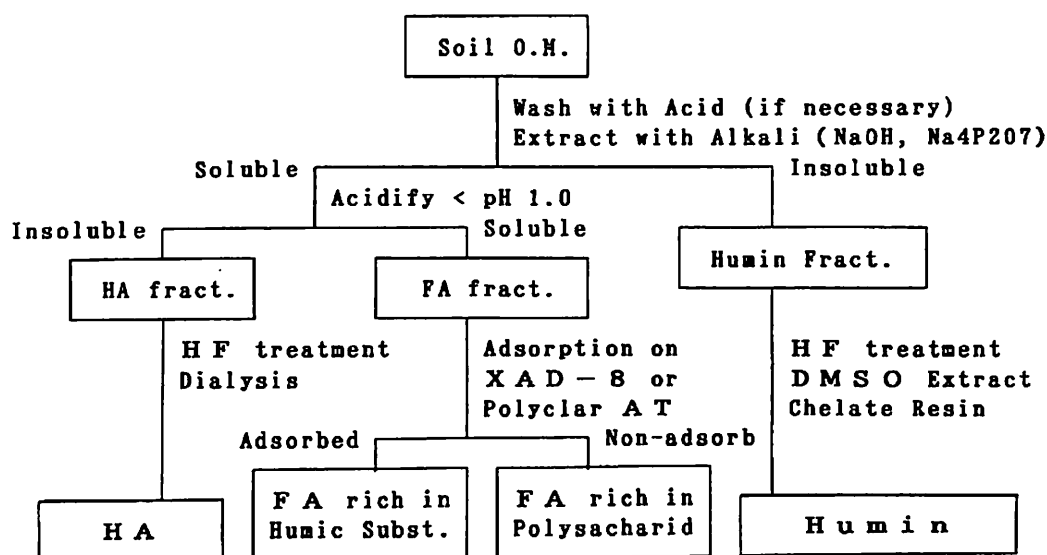


Fig. 3. Fractionation of soil organic matter

5. Pathway of humic substance formation

In what pathway are humic substances formed? This is a very important but difficult question, which many soil scientists and chemists have tackled.

In many soils, lignin is the main source of aromatic units of soil humic acids (Kononova, 1966). This is demonstrated by the fact that most of the labeled carbon of lignin is incorporated into humic acid when it is incubated in soil (Martin and Haider, 1980). Lignin also undergoes significant degradation in soil. The bonds between lignin and cellulose are split, and methoxyl and methyl groups disappear. On the other hand carboxyl groups are formed. Nitrogen content increases as a result of the interaction between the degradation products of lignin and microbial metabolic products. Aromatic rings which appear on the surface of the lignin molecule are broken down microbially and a highly branched aliphatic skeleton is formed.

Tannins also take part in the formation of humic substances (Kononova, 1966). They liberate polyphenol upon degradation, which couple with amino compounds and proteins oxidatively to form a dark colored high polymer.

The similarity between melanin and humic acid is also pointed out on the basis of functional group analysis, pyrolytic products, oxidative and reductive degradation products, and various absorption spectra (Stott and Martin, 1990). Abundance of fungi with melanin forming ability in soil also suggests the contribution of microbial melanin on the formation of soil humic substances.

The mechanisms mentioned above are, however, concerned with the initial process of the

humification. In other words, they occur under the condition that constituents of decaying plant materials and microbial metabolic products exist in large amounts and can readily interact with each other. Highly humified humic acids which are obtained from humic volcanic ash soils (Andisols) and chernozem soils (Mollisols), bear little similarity with lignin, tannin, or melanin.

To explain the occurrence of highly humified humic substances, polymerization of polyphenols and quinones under the catalytic action of clay minerals and sesquioxides should be considered (Fig.4). Once formed, a humic substance also undergoes further changes in structure similar to coalification and acquire a complex structure inherent in soil humic substances.

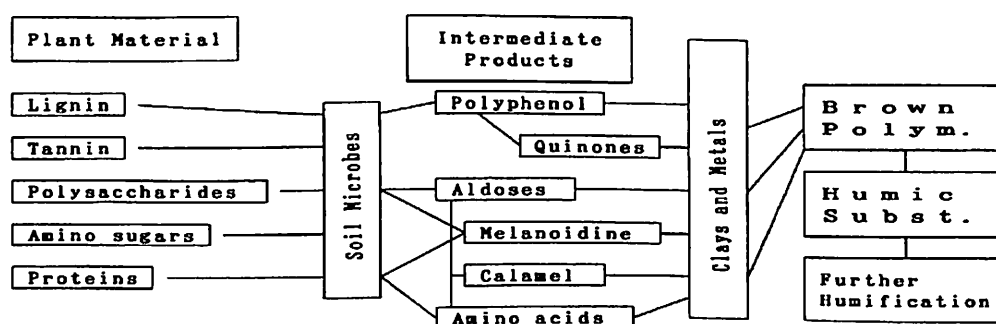


Fig. 4. Constituents of the humification process

6. Chemical composition and properties of the fractions of SOM

6-1. Elementary composition

Elementary composition of humic acid has been studied extensively (Schnitzer and Khan, 1978; Kuwatsuka et al., 1978; Kumada, 1987; Yonebayashi, 1988).

Hydrogen content (H/C) decreases, while the degree of unsaturation (DUS) as calculated from the following equation, increases with the degree of humification (Kuwatsuka et al., 1978; Kumada and Tsutsuki, 1980).

$$DUS = \frac{2[C] + [N] - [H]}{[C]} \times 100$$

where [C], [N], [H] are atomic percentages.

Nitrogen content of humic acids increases in the initial stage of humic acid formation, but it decreases again as the degree of humification increases.

Carbon and oxygen content, however, increase as the degree of humification increases. When compared among differing types of soils, this tendency is obscure, but when compared among similar types of soils or among fractions of humic acids extracted from one soil, this tendency is clear.

Compared with humic acids, fulvic acids have lower amounts of carbon and nitrogen, and a lower degree of unsaturation, while having higher contents of oxygen and hydrogen (Table 2). Compared with the non-adsorbed fraction which is rich in polysaccharides, the fraction adsorbed on Polyclar AT resin has lower H/C and N/C while higher O/H and degree of unsaturation (Watanabe et al., 1993).

Table 2. Elementary and functional group composition of Humic and Fulvic Acids

	Humic Acids Tsutuski et. al	Humic Acids Schnitzer et. al	Fulvic Acids
Elementary composition (%)			
C	53.0 - 60.4	53.6 - 58.7	40.7 - 50.6
H	2.5 - 7.1	3.2 - 6.2	3.8 - 7.0
N	1.1 - 6.9	0.8 - 5.5	0.9 - 3.3
S	N.D.	0.1 - 1.5	0.1 - 3.6
O	29.0 - 39.1	32.7 - 38.3	39.7 - 49.8
Functional Groups (mol Kg ⁻¹)			
Total Acidity	3.6 - 8.5	5.6 - 7.7	6.4 - 14.2
— COOH	2.4 - 6.3	1.5 - 5.7	5.2 - 11.2
Phenolic — OH	0.8 - 3.7	2.1 - 5.7	0.3 - 5.7
Alcoholic — OH	0.2 - 4.4	0.2 - 4.9	2.6 - 9.5
Quinone + Ketone C=O	2.2 - 8.8	0.1 - 5.6	1.2 - 4.2
Methoxyl — OCH ₃	0.1 - 2.6	0.3 - 0.8	0.3 - 1.2

N.D.: not determined

Data for the elementary composition of the humin fraction are rare. According to Kononova (1966), the humic acid isolated by acid treatment from the humin fraction had higher hydrogen and oxygen contents, while having lower carbon contents compared with the humic acid fraction of the same soil. Tsutuski et al. (1992) also showed that the humin sample obtained by DMSO extraction and HF treatment had higher hydrogen content than the humic acids. These results suggest that the humin fraction is rich in aliphatic structure.

6-2. Functional group composition

Fractions of SOM have various types of functional groups, such as carboxyl, carbonyl, phenolic hydroxyl, alcoholic hydroxyl, methoxyl, and amino groups. These functional groups participate significantly in the reactivity of humic substances.

According to Tsutuski et al. (1979), carboxyl group contents of humic acids ranged between

2.5 and 6.3 mol/kg while carbonyl groups between 2.5 and 6.8 mol/kg. Both groups increased as the degree of humification increased. The phenolic hydroxyl group of humic acids (1.9-3.3 mol/kg) decreased in the initial stage of humification, but increased again as the degree of humification increased. Alcoholic hydroxyl group (1.0-5.0 mol/kg) and methoxyl group (0-2.6 mol/kg) decreased as the degree of humification increased, suggesting the decrease in carbohydrate and lignin structure in humic acids.

Compared with humic acids, fulvic acids have much larger amounts of carboxyl and alcoholic hydroxyl groups. Fulvic acids have larger amounts of strong carboxylic acids ($pK < 3.8$) than humic acids. They also contain larger amounts of 1,2 dicarboxylic acids (Arai et al., 1978).

6-3. Nitrogenous constituents

Nitrogen in soil is contained largely in the structure of humic substances. Nitrogen in humic substances is not easily decomposed and is less available to plants.

Nitrogen in humic substances may be divided into the following five fractions after acid hydrolysis with 6 N HCl or by equivalent acids:

- (1) Acid insoluble N,
- (2) NH_3 N,
- (3) Amino acid N,
- (4) Amino sugar N,
- (5) Hydrolysable unknown N.

Among the above, amino acid N and amino sugar N are the most dominant identifiable nitrogenous components. Amino acid composition of humic acids obtained from various soils show a remarkable similarity to each other (Stevenson, 1982, Tsutsuki et al., 1979), suggesting the very similar origin of nitrogen, such as microbial cell walls, in various soils.

Though the content of amino acid N increases in the initial stage of humification, it decreases again with the increasing degree of humification (Tsutsuki and Kuwatsuka, 1979).

Acid non-hydrolysable N occupies 30-60% of the total N in humic acid. Its percentage increases with the increasing degree of humification. It exists in forms of nitrogen in the aromatic or quinone ring, or in N-phenyl amino acid which is formed by the coupling of the terminal N of peptides and an aromatic ring. A similar form of nitrogen also constitutes the acid hydrolysable unknown N, which is contained in large amounts in fulvic acids.

Ammonia in the acid hydrolysate come partly from the amide group of glutamin and asparagin. Ammonia N which can not be explained by amide group is called pseudo-amide N (Aldag, 1977).

6-4. Soil polysaccharides

Soil polysaccharides occupy 5-30% of SOM. They are also contained in large amounts in humic acids and fulvic acids. Polysaccharides containing amino sugars and uronic acids and their metal complexes exist in the humin fraction (Stott and Martin 1990; Cheshire, 1979).

Soil polysaccharides originate from both microbes and plants. Microbial and plant

polysaccharides, however, do not exist in their intact form in soils. During decomposition, they are combined together and acquire the stable structure inherent to soil. This has been inferred from the very complex composition of constitutional monosaccharides of soil polysaccharides. The very high stability of soil polysaccharide is also ascribed to the complex formation of polysaccharides with metals and clay minerals, which render polysaccharides not easily available for microbes. Localized distribution in soil aggregates also protects soil polysaccharides from decomposition.

6-5. Structural information obtained by spectrometry

Various absorption spectra, i.e. UV-Vis., IR, H-NMR, ¹³C-NMR, ESR, X-ray diffraction, and Mössbauer spectra, have contributed to the analysis of the structure of humic substances. Only three of these will be cited here due to lack of space, not because they are most important.

Ultraviolet and visible absorption spectra of humic substances show a simple tone, and exponentially decreasing absorbance with increasing wave length, except for some humic acids containing pigments or less altered plant materials. This exponential curve of UV spectra itself is considered to be an inherent characteristic of soil humic substances. This shows that the dark color of the humic substances comes from the randomly coupled double bond system, and not from any special chromophores. By using the indicators based on UV absorption, the degree of humification of humic acids can be defined, and humic acids can be classified into various types (Kumada, 1987). The chemical characteristics of humic acids shows a very intimate relationship either with the degree of humification or with the types of humic acids.

¹³C-NMR gives a well defined idea on the relative distribution of aromatic and aliphatic structures, polysaccharides, carboxyl and carbonyl carbons in SOM fractions (Wilson, 1990). This technique can also be applied to the SOM without isolating it from soil. A recent finding by this technique is that aromatic carbon in humic acids rarely exceeds 50% of their total C, while the proportion of aliphatic carbon is considerably high. An extreme case is the organic matter isolated from an interlayer clay-organic complex found by Theng et al. (1986). The organic material intercalated between the mica-beidellite lattice was composed almost solely of alkyl carbon and contained no aromatic carbon. The contribution of polysaccharide carbon to SOM has also been distinctly shown.

X ray diffraction analysis of humic acids has shown that the highly humified humic acids (A type HA) have a turbo-stratic structure similar to amorphous graphite carbon (Kumada, 1987). Electron microscopic observation also confirmed this. In the turbo-stratic structure, several condensed aromatic ring structures are piled up on each other. Other spectrometric techniques failed to prove this evidence.

Various spectrometric procedures sometimes give contradictory information on the structure of humic substances. This is inevitable due to the difference in the principle of each spectrometry as well as to the heterogeneity of humic substances.

6-6. Molecular weight, size and shape

Molecular weights of humic acids, fulvic acids, and polysaccharides range from ca. 500 to

several million. A molecule of humic acid is large while that of fulvic acid is small. According to Tsutsuki et al. (1989), the average molecular weight of humic acids ranged from 200,000 to 2,000,000. The molecular weight was smaller in A type humic acid with a high degree of humification and larger in Rp type humic acids with a lower degree of humification. Average molecular weight of fulvic acid is ca. 20,000 and varied little among different soils (Watanabe et al., 1992). They also showed that the fulvic acid adsorbed on the Polyclar AT resin, which is rich in humic substances, had smaller molecular weight (17,100-19,700) than the non-adsorbed fraction rich in polysaccharides (21,800-26,500).

The tendency of the molecular weight of humic acid to decrease with the increasing degree of humification may seem contradictory to the process of humic acid formation, which assumes the coupling of low molecular polyphenols and quinones into high molecular humic substances. However, the molecular weight of the humic acid formed in the initial stage of humification, having the lignin structure as its core, may have much larger molecular weight than the humic substances synthesized in the later stage of humification.

The molecular shape of humic acids and fulvic acids changes readily according to environments. This is shown by the dependency of the gel permeation chromatogram on the pH or on the ionic strength of the eluent solution (Tsutsuki et al., 1984). Large contents of carboxyl groups in humic acids and fulvic acids as well as the recent findings by ^{13}C -NMR that aliphatic structure exists abundantly in humic substances, corresponds with the variable molecular shape of humic substances. The molecular shape of humic acids can be well explained by the behavior of the linear polyelectrolytes which are flexible random chains with a spherical ellipsoidal shape as a whole.

7. Functions of SOM in relation to agricultural practice

As mentioned above SOM is composed of various components, each of which has different characteristics and functions. With respect to its effect on plant growth, the effect caused solely by organic matter is rare. In co-operation with soil microbes and soil mineral components, SOM influences the growth of plants. This is why the amount of SOM does not always solely prove the high productivity of the soil. The roles of SOM on soil fertility can be divided into direct and indirect effects.

7-1. Direct effects

Under the existence of adequate mineral nutrients, humic substances (humic acids and fulvic acids) very often show positive effects on the growth of plants. Effects are observed in germination, seedling growth, root initiation and growth, and shoot development (Chen and Aviad, 1990). The effect is usually more prominent on the growth of the root than on the growth of the shoot. There is an optimum level of humic substances for maximum effect. Too high a level exerts negative effects. Foliar sprays can also enhance both root and shoot growth.

The mechanism of plant growth stimulation are related to the enhanced uptake of

macroelements and microelements. Humic substances form complexes with transition metals. Metal ions existing in unavailable form may be converted to available form by complex formation. This promotes the absorption of these metals by plants. In case of metal ions existing in excess amounts complex formation reduce their toxicity. Low molecular weight constituents in humic substances may be absorbed directly by plants. They exert a hormone like action, and promote the permeability of the cell membrane.

7-2. Indirect effects

Indirect effects of SOM are summarized as follows.

- 1) Dark color of humic substances promotes the absorption of solar energy and keeps the soil warm.
- 2) Improvement of soil physical properties and stabilization of soil structure by promoting the aggregate formation. Hyphae of fungi, polysaccharides, and humic substances all participate in the formation of soil aggregates. However, the aggregate formed by humic substances is the most stable and durable.
- 3) Supporting the mineral nutrients by its cation exchange capacity. In many soils, soil organic matter is responsible for 20-70% of the total CEC of the soil. In the tropical and subtropical region, where intense weathering of clay minerals occurs, contribution of organic matter is important.
- 4) Buffer action against drastic pH change.
- 5) The source of N, P, S, and other essential elements. During the decomposition, these elements pass through the microbial biomass and are transferred to plants.
- 6) Nutrient source for soil microbes. There are vast kinds of microbes, which all differ in their nutritional demands. SOM satisfies the various nutritional demands of soil microbes by its heterogeneity. The abundant and heterogeneous microbial flora provides an abundant nutrient supply to plants and also functions as a biological buffer against the change in soil environments caused by human activities. They also prevent the spread of soil-borne disease.

Thus, SOM plays a very important role in keeping the soil fertile. Because its effects are not so prominent as those of fertilizers and agricultural chemicals, the importance of SOM is easily forgotten in modern agriculture. SOM, however, is lost yearly under the usual cultivation practice of modern agriculture. This will cause serious decrease in soil productivity and the loss of arable soil itself by erosion within a few decades. Organic matter application to arable soils is what we learned from the process of nature. It is indispensable to extend the life (SOM) of arable soil.

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