

# **ORGANIC MATTER, HUMUS, HUMATE, HUMIC ACID, FULVIC ACID, AND HUMIN:**

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## **INTRODUCTION**

Humic substances, such as those listed in the above title, play a vital role in soil fertility and plant nutrition. Plants grown on soils which contain adequate humin, humic acids (Has), and fulvic acids (Fas) are less subject to stress, are healthier, produce higher yields; and the nutritional quality of harvested foods and feeds are superior. The value of humic substances in soil fertility and plant nutrition relates to the many functions these complex organic compounds perform as a part of the life cycle on earth. The life-death cycle involves a recycling of the carbon containing structural components of plants and animals - through the soil and air - and back into the living plant

Man became distracted from the importance of organic compound cycling when it was discovered that soluble acidic based N-P-K "fertilizers" could stimulate plant growth. Large industrial concerns took advantage of the N-P-K discovery to market industrially processed "fertilizers" from mineral deposit. Continued use of these acidic fertilizers in the absence of adequate humic substance (in the soil) has caused many serious sociological and ecological problems. Man needs to reconsider his approach to fertilization techniques by giving higher priority to soil humus.

The urgency to emphasize the importance of humic substances and their value as fertilizer ingredients has never been more important than it is today. All those concerned about the ability of soils to support plant growth need to assist in educating the public. Humic substances are recognized by most soil scientists and agronomists as the most important component of a healthy fertile soil. To illustrate how humic substances function, the following summary, based on published scientific data, has been prepared as a guide for an educational program. In addition, by understanding how these carbon containing substances function, professionals will have a solid foundation on which to design environmentally acceptable sustainable agriculture programs.

## **DESCRIPTION OF TERMS USED IN THE SUMMARY**

A brief discussion of several important terms will help clarify to the reader the significance of humic substances, and how scientists have subdivided and described specific extracts from these substances. Key features of these extracts have been discovered as agriculturists have worked to understand the structural and functional properties of humic substances.

**ORGANIC MATTER** - Organic matter is defined as a grouping of carbon containing compounds which have originated from living beings and been deposited on or within the earth's structural components. Soil organic matter includes the remains of all plant and animal bodies which have fallen on the earth's surface or been purposely applied by man in the form of organically synthesized pesticides. A fertile soil should contain from 2-8 percent organic matter; most soils contain less than 2%. In acid, leached soils, which are often sandy, substantial portions of the organic matter is in the form of plant debris and fulvic acids (FAs). In neutral and alkaline soils a large percentage of the organic matter is in the form of humic acids (HAs) and humin.

When organic matter is burned, there remains a residual ash. The residual ash is composed of the minerals, trace elements required by plants and animals during their normal growth processes. Thus organic matter contains mineral elements required by plants

An accurate measurement of the soil would be helpful in monitoring soil fertility. Currently the best extractant for removing organic matter from a soil is 0.5 normal sodium hydroxide (NaOH) (working under N<sub>2</sub>). The second best extractant is sodium pyrophosphate decahydrate (Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> 10H<sub>2</sub>O (pH 9.8)). Neither one of these extractants is able to remove all of the organic matter from a soil sample. Obviously since these chemicals are the best known it is impossible to determine the exact amount of organic matter present within a soil. In reality soil organic matter is not a measurable soil component. The organic matter content of a soil sample, reported on soil tests, is only an estimate. The organic carbon content of a soil can be measured and would be a much more valuable indication of the potential humic-chemistry of a soil. The soil's carbon content would be a desirable part of a soil test report.

**HUMUS** - Humus is defined as a brown to black complex variable of carbon containing compounds not recognized under a light microscope as possessing cellular organization in the form of plant and animal bodies. Humus is separated from the non-humic substances such as carbohydrates (a major fraction of soil carbon), fats, waxes, alkanes, peptides, amino acids, proteins, lipids, and organic acids by the fact that distinct chemical formulae can be written for these non-humic substances. Most small molecules of non-humic substances are rapidly degraded by microorganisms within the soil. In contrast soil humus is slow to decompose (Degrade) under natural soil conditions. When in combination with soil minerals soil humus can persist in the soil for several hundred years. Humus is the major soil organic matter component, making up 65% to 75% of the total. Humus assumes an important role as a fertility component of all soils, far in excess of the percentage contribution it makes to the total soil mass.

**HUMIC SUBSTANCES** - humic substances are the components of humus and as such as high molecular weight compounds that together form the brown to black hydrophilic, molecularly flexible, polyelectrolytes called humus. Many of the components of humus are heterogeneous, relatively large stable organic complexes. They function to give the soil structure, porosity, water holding capacity, cation and anion exchange, and are involved in the chelation of mineral elements. The elemental analysis of humic substances reveals that they are primarily composed of carbon, oxygen, hydrogen, nitrogen, and sulfur in complex carbon chains (aliphatic components that make up approximately 40% - 50% of the total) C-C-C-C and 4, 5, and 6 member carbon rings (aromatic components that make up 35% - 60% of the total) with C-C, C-N, and C=O groupings.

Preliminary understandings about how humic substances are formed is based on 4 published theories: (1) Lignin modifications, (2) Quinone -Amino Acid Interaction, (3) Microbial Synthesis of Aromatics, and (4) The Mallard Reaction (a sugar - amino acid reaction sequence). Each theory describes complicated biotic and abiotic reactions in which a variety of organic compounds, such as phenolic compounds (e.g. lignins), complex carbohydrates, and nitrogenous substances are resynthesized to form large complex polymers. In order for these polymerization reactions to proceed, inorganic mineral catalysts must be present. Therefore, the availability of trace minerals is a requirement for the formation of humic substance. The extreme variability in the molecular features of humic substances relates back to the precursor compounds and the environmental conditions under which the humic substances formed.

Humic substances have been shown to contain a wide variety of molecular components. Some typical components are: polysaccharides; fatty acids; polypeptides; lignins; esters; phenols; ethers; carbonyls; quinones; lipids; peroxides; various combinations of benzene, acetal, ketal, and lactol, and furan ringed compounds; and aliphatic (carbon chains) compounds. The oxidative degradation of some humic substances produces aliphatic, phenolic, and benzene carboxylic acids in addition to n-alkanes and n-fatty acids. The major phenolic acids released contain approximately 3 hydroxyl (-OH) groups and between 1 and 5 carboxyl (-COOH) groups.

Humic substances can be subdivided into three major fractions (1) HUMIN, (2) HUMIC ACIDS (Has), and (3) FULVIC ACIDS (Fas). These sub-divisions are arbitrarily based on the solubility of each fraction in water adjusted to different acid - alkaline (pH levels) conditions. Some of the major features of humic substances are summarized in Figure 1.

**HUMINS** - Humins are that fraction of humic substances which are not soluble in alkali (high pH) and are not soluble in acid (low pH). Humin are not soluble in water at any pH. Humin complexes are considered macro-organic (very large) substances because their molecular weights (MW) range from approximately 100,000 to 10,000,000. In comparison the molecular weights of carbohydrates (complex sugars) range from approximately 500 to 100,000. The chemical and physical properties of humins are only partially understood. Humins present within the soil is the most resistant to decomposition (slow to breakdown) of all the humic substances. Some of the main functions of humins within the soil are to improve the soils water holding capacity, to improve soil structure, to maintain soil stability, to function as a cation exchange system, and to generally improve soil fertility. Because of these important functions humin is the key component of fertile soils.

**HUMIC ACIDS** - Humic acids (HAs) comprise a mixture of weak aliphatic (carbon chains) and aromatic (carbon rings) organic acids which are not soluble in water under acid conditions but are soluble in water under alkaline conditions. Humic acids consist of that fraction of humic substances that are precipitated from aqueous solution when the pH is decreased below 2.

Humic acids (HAs) are termed polydisperse because of their variable chemical features. From a three dimensional aspect these complex carbon containing compounds are considered to be flexible linear polymers that exist as random coils with cross-linked bonds. On average 35% of the humic acid (HA) molecules are aromatic (carbon rings), while the remaining compounds are in the form of aliphatic (carbon chains) molecules. The molecular size of humic acids (HAs) range from approximately 10,000 to 100,000. Humic acid (HA) polymers readily bind clay minerals to form stable organic-clay complexes. Peripheral pores in the plant are capable of accommodating (binding) natural and synthetic organic chemicals in a lattice (clathrate) type arrangement.

Humic acids (HAs) readily form salts with inorganic trace mineral elements. An analysis of extracts of naturally occurring humic acids (HAs) will reveal the presence of over 60 different mineral elements present. These trace elements are bound in humic acid molecules in a form that can be readily utilized by various living organisms. As a result humic acids (HAs) function as important ion-exchange and metal-complexing (chelating) systems.

**FULVIC ACIDS** - fulvic acids (FAs) are a mixture of weak aliphatic and aromatic organic acids which are soluble in water at all pH conditions (acidic, neutral and alkaline). Their composition and shape is quite variable. The size of fulvic acids (FAs) are smaller than humic acids (HAs), with molecular weights which range from approximately 1,000 to 10,000. Fulvic acids (FAs) have an oxygen content twice that of humic acids (HAs). They have many carboxyl (-COOH) and hydroxyl (-COH) groups, thus fulvic acids (FAs) are much more chemically reactive. The exchange capacity of fulvic acids (FAs) is more than double that of humic acids (HAs). This high exchange capacity is due to the total number of carboxyl (-COOH) groups present. The number of carboxyl groups present in fulvic acids (FAs) ranges from 520 to 1120 cmol (H+)/kg. Fulvic acids collected from many different sources and analyzed, show no evidence of methoxy (-CH<sub>3</sub>) groups, they are low in phenols, and are less aromatic compared to humic acids from the same sources.

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Because of the relatively small size of fulvic acids (FA) molecules they can readily enter plant roots, stems, and leaves. As they enter these plant parts they carry trace minerals from plant surfaces into plant tissues. Fulvic acid (FAs) are key ingredients in high quality foliar fertilizers. Foliar spray applications containing fulvic acid (FA) mineral chelates, at specific plant growth stages, can be used as a primary production technique for maximizing the plants productive capacity. Once applied to plant foliage fulvic acids (FAs) transport trace minerals directly to metabolic sites in the plant cells. Fulvic acids (FAs) are the most effective carbon containing chelating compounds known. They are plant compatible, thus non-toxic, when applied at relatively low concentrations.

**HUMATES** - Humates are metal (mineral) salts of humic (HAs) or fulvic acids (FAs). Within any humic substance there are a large number of complex humate molecules. The formation of a humate is based on the ability of the carboxyl (-COOH) and hydroxyl (-OH) groups (on the outside of the polymers) to dissociate (expel) the hydrogen ion. Once the hydrogen ions dissociated a negatively charged anion (-COO<sup>-</sup> or -CO<sup>-</sup>) results. Two of these anions can bind to positive metal cations, such as iron (Fe<sup>++</sup>), copper (Cu<sup>++</sup>), zinc (Zn<sup>++</sup>), calcium (Ca<sup>++</sup>), manganese (Mn<sup>++</sup>), and magnesium (Mg<sup>++</sup>). The simplified reaction (-COO<sup>-</sup> + Fe<sup>++</sup> >> -COOFe<sup>+</sup> + H) proceeds to bind two anions, frequently a -COOH and a -COH group. The humate composition of any one humic substance is specific for that substance. Thus there exists a large variability in the molecular composition of different humic substances. Humates from different mineral deposits would be expected to have their own unique features.

## HUMIC SUBSTANCES AND THEIR INFLUENCE ON SOIL FERTILITY

Humic substances are a good source of energy for beneficial soil organisms. Humic substances and non-humic (organic) compounds provides the energy and many of the mineral requirements for soil microorganisms and soil animals. Beneficial soil organisms lack the photo synthetic apparatus to capture energy from the sun thus must survive on residual carbon containing substances on or in the soil. Energy stored within the carbon bonds function to provide energy for various metabolic reactions within these organisms. Beneficial soil organisms (algae, yeast, bacteria, fungi, nematodes, mycorrhizae, and small animals) perform many beneficial functions which influence soil fertility and plant health. For example the bacteria release organic acids which aid in the solubilization of mineral elements bound in soil. Bacteria also release complex polysaccharides (sugar based compounds) that help create soil crumbs (aggregates). Soil crumbs give soil a desirable structure. Other beneficial soil microorganisms such as the Actinomyces release antibiotics into the soil. These antibiotics are taken up by the plant to protect it against pests. Antibiotics also function to create desirable ecological balances of soil organisms on the root surface (rhizoplane) and in soil near the root (rhizosphere). Fungi also perform many beneficial functions in soils. For example, micorrhizae aid plant roots in the uptake of water and trace elements. Other fungi decompose crop residues and vegetative matter releasing bound nutrients for other organisms. Many of the organic compounds released by fungi aid in forming humus and soil crumbs. Beneficial soil animals create tunnel-like channels in the soil. The channels allow the soil to breath, and exchange gases with the atmosphere. Soil animals also aid in the formation of humus, and help balance the concentration of soil microorganisms. A healthy fertile soil must contain sufficient carbon containing compounds to sustain the billions of microscopic life forms required for a fertile and a healthy plant. A living soil is a fertile healthy soil.

Humus functions to improve the soil's water holding capacity. The most important function of humic substances within the soil is their ability to hold water. From a quantitative standpoint water is the most important substance derived by plants from the soil. Humic substances help create a desirable soil structure that facilitates water infiltration and helps hold water within the root zone. Because of their large surface area and internal electrical charges, humic substances function as water sponges. These sponge like substances have the ability to hold seven times their volume in water, a greater water holding capacity than soil clays. Water stored within the top-soil, when needed, provides a carrier medium for nutrients required by soil organisms and plant roots.

Available water is without doubt the most important component of a fertile soil. Soils which contain high concentrations of humic substances hold water for crop use during periods of drought. This is why growers who apply humate-based fertilizers and integrate production practices which preserve humic substances, can frequently harvest a crop during periods of dry weather.

Humic substances are key components of a friable (loose) soil structure. Various carbon containing humic substances are key components of soil crumbs (aggregates). Complex carbohydrates synthesized by bacteria and humic substances function together with clay and silt to form soil aggregate. As the humic substances become intimately associated with the mineral fraction of the soil, colloidal complexes of humus-clay and humus-silt aggregates are formed. These aggregates are formed by electrical processes which increase the cohesive forces that cause very fine soil particles and clay components to attract each other. Once formed these aggregates help create a desirable crumb structure in the top soil, making it more friable. Soils with good crumb structure have improved tilth, and more porous openings (open spaces). These pores allow for gaseous interchange with the atmosphere, and for greater water infiltration.

The mean residence times of these organo-mineral complex aggregates varies with different humic substances. The mean residence time of humic substances within these aggregates, based on radiocarbon dating, using extracts from non-disturbed soil, is as follows: humin, 1140 years; humic acid, 1235 years; and fulvic acid, 870 years. Man has shortened the residence time of humic substances by excessive fertilizing and by using tilling practices that cause excessive weathering of soils. Soils abused by applications of anhydrous ammonia and by other destructive practices (those which destroy humic substances) can shorten residence times by several hundred years. The turnover time of organic carbon added each year from plant and animal residues averages approximately 30 years, under ideal conditions. In order to retain humic substances within the soil growers need to implement production practices which prevent their decomposition. Growers need to develop practices which retain the residence time of humic substances. It is essential to avoid destructive fertilization practices, rotate crops, minimize pesticides usage, deep plowing, and mix crop residues in the top soil by using minimum tillage practices. Soils which contain adequate humic substances have improved tilth (work ability) and are thus more efficiently maintained for crop production.

Degradation or inactivation of toxic substances is mediated by humic substances. Soil humic substances function to either stabilize or assist in the degradation of toxic substances such as: nicotine, aflatoxin, antibiotics, phenols, and most organic pesticides. In the microbial degradation process not all of the carbon contained within these toxins is released as CO<sub>2</sub>. A portion of these toxic molecules, primarily the aromatic ring compounds are stabilized and integrated within the complex polymers of humic substances. Humic substances have electrically charged sites on their surfaces which function to attract and inactivate pesticides and other toxic substances. For this reason the Environmental Protection Agency recommends the use of humates for clean up of toxic waste sites. Many bioremediation companies apply humate based compounds to toxic

waste sites as a part of their clean up program. Growers interested in cleaning up their soils (destroying various toxic pesticides) can accelerate the degradation of poisons (toxins) by applying humic substances. Growers who farm soils low in humus need to include the purchase of humic substances in their fertilizer budget. The cost of humic substances can be more than offset by reduced costs of other fertilizer ingredients.

Humic substances buffer (neutralize) the soil pH and liberate carbon dioxide. Humic substances function to buffer the hydrogen ion (pH) concentration of the soil. Repeated field studies have provided experimental evidence that the addition of humic substances to soils helps to neutralize the pH of those soils. Both acidic and alkaline soils are neutralized. Once the soil is neutralized, then many trace elements formerly bound in the soil and unavailable to plant roots, because of alkaline or acidic conditions, become available to the plant roots. Humic substances also liberate carbon dioxide (CO<sub>2</sub>) from calcium carbonates present within the soil. The released CO<sub>2</sub> may be taken up by the plant or it may form carbonic acids. The carbonic acids act on soil minerals to release plant nutrients.

Soil enzymes are stabilized and inactivated by humic substances. Soil enzymes (complex proteins) are stabilized by humic substances within the soil by covalent bonding. Stabilization renders these enzymes less subject to microbial degradation. Once stabilized and bound to the humic substances enzyme activity is greatly reduced or ceases to function. However many of these bonds are relatively weak. During periods of pH change within the soil, these enzymes can be released. When some components of humic substance react with soil enzymes they are more tightly bound. For example, phenolic-enzyme complexes are frequently attached to clays, further stabilizing the enzymes. These enzyme stabilization processes help to restrict the activity of potential plant pathogens. As the potential plant pathogen release enzymes designed to break down the plant's defenses, the pathogens enzymes become bound to humic substances. As a result the pathogens are unable to invade potential host plants.

Soil temperatures and water evaporation rate are stabilized by humic substances. Humic substances function to help stabilize soil temperatures and slow the rate of water evaporation. The insulating properties of humic substances help maintain a more uniform soil temperature, especially during periods of rapid climate changes, such as cold spell or heat waves. Because water is bound within the humic substances and humic substances reduce temperature fluctuations, soil moisture is less likely to be released into the atmosphere.

The electrical features of humic substances influence known chemical reactions. Both groups of complex organic acids, humic acids (HAs) and fulvic acids (FAs) have been proven to be involved in three specific chemical reactions. These reactions are commonly termed: (1) electrostatic (columbic) attraction, (2) complex formation or chelation, and (3) water bridging.

Electrostatic attraction of trace minerals reduces leaching into subsoil. Electrostatic attraction of metal cations to anionic sites on the humic substance keeps these ions from leaching into the subsoil. The metal cation is loosely attached, thus can be released when attracted to another stronger electrical charge. The cation is readily available in the soil environment for transport into the plant roots or exchanged for another metal cation

Electrically charged sites on humic substances function to dissolve and bind trace minerals. When a complex reaction with metal cations occurs on the humic substance surface it is termed chelation. Two negatively charged sites on the humic substance attract metal cations with two negative charges. As a result the cation binds itself to more than one charged anionic site. By forming organo-metal chelates, these organic acids bring about the dissolution of primary and secondary minerals within the soil. These minerals then become available for uptake by plant roots. The greater the affinity of the metal cation for humic acid (HA) or fulvic acid (FA), the easier the dissolution of the cation from various mineral surfaces. Both the acidic effects and the chelation effects appear to be involved in dissolution of minerals and binding processes. Evidence for the dissolution of minerals can be supported by x-ray diffraction and infrared analysis. Chelation of plant nutrients such as iron (Fe), copper (Cu), zinc (Zn), magnesium (Mg), manganese (Mn), and calcium (Ca) reduces their toxicity as cations, prevents their leaching, and increases their uptake rate by plant roots.

The chelation exchange reaction involves a transition element. The release of these trace minerals into the plant is quite different from the classical cation exchange system. The cation with a plus two charge, present in the chelate, cannot be replaced by a singly charged cation such as H<sup>+</sup>, K<sup>+</sup> or Na<sup>+</sup>. Cations with one positive charge are unable to replace a metal ion, such as Cu<sup>++</sup>, with two positive charges. The chelated metal ion can be exchanged by another transitional ion that has two positive charges. The chelates provide the carrier mechanism by which depleted nutrient elements are replenished at the root surface. The chelation process also increases the mass flow of micro nutrient mineral elements of the root. The chelation of heavy toxic metallic elements present within the soil is also influenced by humic substances present. When toxic heavy metals such as mercury (Hg), lead (Pb), and cadmium (Cd) are chelated these organo-metal complexes become less available for plant uptake. Detailed studies of chelation of heavy metals in industrial sludge has illustrated the value of humic substances in preventing uptake of these toxic metals. Keep in mind that free metal cations such as Fe<sup>+2</sup>, Cu<sup>+2</sup>, and Zn<sup>+2</sup> are incompatible with plant cells. Direct applications of metallic salts, such as iron sulfate, copper sulfate, and zinc sulfate, to correct trace element deficiencies, can cause serious problems when the soils lack sufficient humic substances for buffering. Trace minerals should be applied in an organic chelate, preferably by humic acids (HAs) and fulvic acids

(FAs). Many scientific studies have shown that humic substances [humic acids (HAs) fulvic acids (FAs)] present in the root zone reduce the toxicity of metal cations.

Water bridging is an important function of humic and fulvic acids. Water bridging by humic substances involves the attraction of a water molecule followed by the attraction of a mineral element cation (Simply illustrated by  $(-\text{COO}^- - \text{H}_2\text{O} - \text{Fe}^{+})$  at an anionic site on the humic (HA) or fulvic acid (FA) polymers. The water holding capacity of humic substances and their ability to bind trace mineral elements function together in water bridging. Water bridging is believed to improve the mobility of nutrient ions through the soil solution to the root. These mechanisms also help reduce leaching of plant nutrients into the subsoil. Recent experiments indicate that water bridging may be more common in humic substances than originally believed.

Humic substances aid in the decomposition of soil minerals by forming metal-organic-clay complexes, a process termed soil genesis. Soil formation (soil genesis) involves a complexing of transition mineral elements, such as copper (Cu), zinc (Zn), iron (Fe), and manganese (Mn) from soil minerals with humic acids (HAs), fulvic acids (FAs) and clays. This complexing process inhibits crystallization of these mineral elements. The complexing process is in part controlled by the acidity of these weak acids and the chelating ability of humic substances. In the absence of humic substances trace minerals elements are converted to insoluble precipitates such as metal carbonates, oxides, sulfides, and hydroxides. Thus the presence of humic acids (HAs) and fulvic acids (FAs) within soil inhibit the development of new soil minerals. For example, crystallization of iron to form iron oxides is inhibited by the presence of humic acids (HAs) and fulvic acids (FAs). Soils deficient in humic substances may contain adequate iron, however the iron present is frequently bound in forms which render it unavailable to plant roots. As the concentration of fulvic acids (FAs) increases within a soil. Transition metal crystallization is first delayed and then inhibited at high fulvic acid (FA) concentrations. Cations of these transition metals (e.g.  $\text{Cu}^{++}$ ,  $\text{Zn}^{++}$  and  $\text{Fe}^{++}$ ) are held in large humic polymers by chelation, for future release to soil organisms on plant roots. These physical and chemical processes prevent leaching of plant nutrients into the subsoil.

Stored energy and trace mineral content of humic substances helps sustain soil organisms involved in transmutation. The presence of humic substances within saline soils (those soils which contain high salt concentrations, e.g. sodium chloride) aid in the transmutation of the sodium ions. The transmutation reactions, a biological process that occurs within living organisms, result in the combining of sodium with a second element, such as oxygen, to form a new element. Although the theory of transmutation has met considerable opposition by some traditional physicists and chemists, biologist have recorded convincing data to prove that transmutation occurs in living organisms. Application of humins, humic acids, and fulvic acids to saline soils, in combination with specific soil organisms, results in a reduction in the concentration of sodium salts (e.g. NaCl). The reduction is not correlated with a leaching of the salt, rather with an increase in concentration of further elements. The addition of humic substances to soils containing excessive salts can help reduce the concentration of those salts. By reducing the salt content of a soil its fertility and health can be "brought back" to provide a more desirable environment for plant root growth.

## **HUMIC SUBSTANCES AND THEIR INFLUENCE ON PLANT GROWTH AND DEVELOPMENT**

Plant growth is influenced indirectly and directly by humic substances. Positive correlations between the humus content of the soil. Plant yields and product quality have been published in many different scientific journals. Indirect effects, previously discussed, are those factors which provide energy for the beneficial organisms within the soil, influence the soil's water holding capacity, influence the soil's structure, release of plant nutrients from soil minerals, increased availability of trace minerals, and in general improved soil fertility. Direct effects include those changes in plant metabolism that occur following the uptake of organic macromolecules, such as humic acids, fulvic acids. Once these compounds enter plant cells several biochemical changes occur in membranes and various cytoplasmic components of plant cells. Some of the biochemical improvements in plant metabolism, as influenced by humic substances, are summarized in Figure 2.

Uptake of major plant nutrients is mediated by humic substances. One stimulative effect of humic substances on plant growth is enhanced uptake of major plant nutrients: nitrogen (N), phosphorus (P), and potassium (K). When adequate humic substances are present within the soil the requirement for N-P-K fertilizer applications is reduced. As the level of humic substances in soils become depleted the misleading demand for higher concentrations of N-P-K results. Many growers have over the past several years reported increasing demands for soluble acid fertilizers in order to maintain crop yields. Such observations indicate something is wrong within the soil. Increased leaching of nitrate fertilizer ingredients into the ground water is also a warning of problems to come. These trends reflect losses in soil humic substances. Growers could reduce their fertilizer requirements and retain the fertilizer ingredients within the plants rooting zone by the application of humate based fertilizers. The application of either dry or liquid humic substances to soils dramatically increases fertilizer efficiency. Other researchers have reported increased uptake of calcium (Ca), and Magnesium (Mg)

when plants are irrigated with liquid suspensions of humic acids (HAs) or fulvic acids (FAs). Another key mechanism, which maximizes fertilizer efficiency and relates to a function of humic substances, is a reduction in the toxicity and leaching of nitrogen compounds into subsoil water. Humic substances hold these major plant nutrients in a molecular form which reduces their solubility in water. These binding processes reduce leaching nitrogen into the subsoil and help prevent volatilization into the atmosphere.

The absorption of humic substances into seeds has a positive influence on seed germination and seedling development. The application of humic (HA) or fulvic acids (FA) to seeds will increase the seed germination; resulting in higher seed germination rates. Application rates of humic acids (HAs) or fulvic acids (FAs), required for improved seed germination, range from 20 to 100 mg/liter of seed. In order for improved germination to occur the humic substances must be present within the cells of seeds. As the humic substances enter the seed cells, respiration rate increases, and cell division processes are accelerated. These same respiratory processes enhance root meristem development and activate other growing points within the seedlings. Humic substances have been demonstrated to enhance mitotic activity during cell division under carefully controlled experiments. Placement of these humic substances on seed (seed treatment) or within the seed furrow will significantly improve seed germination and seedling development. Excessive concentrations of humic acids (HAs) and/or fulvic acids (FAs) can inhibit seed germination and at high concentrations can kill young seedlings. Therefore follow recommended rates when applying humic substances.

Humic substances have a very pronounced influence on the growth of plant roots. When humic acids (HAs) and/or fulvic acids (FAs) are applied to soil, enhancement of root initiation and increased root growth are observed. Thus the common observation that humic acids (HAs) and fulvic acids (FAs) are root stimulators. In most experimental studies plant root growth is stimulated to a greater extent compared to stimulation of aboveground plant parts. Carefully designed experiments have been conducted under controlled conditions to measure plant responses. For example, replicate treatments of plants grown within the greenhouse, with and without humic acids and fulvic acids has illustrated how humic substances influence root growth. In treated root weights averaged from 20 to 50% heavier compared to the weights of non-treated roots. The type of humic substances applied had a significant influence on the percent of increase. Not all humic substances contain a desirable molecular mixture of humins, humic acids (HAs) and fulvic acids (FAs) capable of rapid stimulation root growth. Some humic substances, because of their large molecular sizes, failed to stimulate plant root development. Root stimulation occurs when the smaller molecular components within fulvic acids (FA) occur at a concentration which ranges from 10 to 100 mg/liter of solution. Growth is further stimulated when fulvic acids (FAs) are used in combination with HUMIC acids (HAs) and other required plant nutrients. Humic substances improve plant nutrition, however they are not complete nutrients by themselves. Excessively high concentrations of humic substances can result in a reduction in root weight. For optimum plant growth humic acids (HAs) and fulvic acids (FAs) should be applied at relatively low concentrations. Application of HUMIC substances within a fairly wide range of concentrations are highly beneficial to plant root development.

Humic acids (HAs) and fulvic acids (FAs) are excellent foliar fertilizer carriers and activators. Application of humic acids (HAs) or fulvic acids (FAs) in combination with trace elements and other plant nutrients, as foliar sprays, can improve the growth of plant foliage, roots, and fruits. By increasing plant growth processes within the leaves an increase in carbohydrates content of leaves and stems occurs. These carbohydrates are then transported down the stems into the roots where they are in part released from the root to provide nutrients for various soil microorganisms on the rhizoplane and in the rhizosphere. The microorganisms then release acids and other organic compounds which increase the availability of plant nutrients. Other microorganisms release "hormone-like" compounds which are taken up by plant roots. The required concentration of humic acids (HAs) and/or fulvic acids (FAs) within the foliar spray should be relatively low, generally less than 50 mg of concentrated dry humic substance per liter of water. Foliar fertilizers containing humic acids (HAs) and fulvic acids (FAs) on combination with nitrogen, potassium, phosphorus and various trace minerals have been demonstrated to be from 100 to 500% more efficient compared to applications of similar fertilizers to the soil. Foliar fertilizers are also more economical because smaller quantities of fertilizer are required to obtain significant plant response. Plant nutrients within foliar fertilizers are rapidly absorbed by the plant leaves. Within 8 hours after applications of humic substances are applied, changes in many different metabolic processes are detected. Enhanced carbohydrates production can be detected within 24 to 48 hours after foliar feeding by use of a refractometer. Enhanced carbohydrate production can either result in improved product quality or increased yields.

Young plant roots, and growing plants are more responsive to applications of humic substances. Actively growing plant tissues are the most responsive to applications of humic substances. Younger tissues have active transport mechanisms that move the required nutrients to sites of metabolic activity. For example, foliar applications of humic substances to young actively growing leaves results in a greater increase in plant growth when compared to foliar applications to older plant leaves. Actively growing plant parts involved in cell divisions and other growth processes, readily integrate various trace minerals and growth regulating compounds into on-going metabolic processes. In contrast older plant parts in which metabolic processes have slowed are unable to efficiently utilize added humic substances and associated nutrients. The concentrations of dry humic acids (HAs) within the spray solution should range from 5 to 100 mg per liter of water for optimum response. Differences in the active ingredients of a specific substances may require changing these concentrations. At higher concentrations, above 100 mg of dry humic acids (HA) per liter, plant, shoot, and even root

growth may be inhibited, depending on the substances under test. Plants respond more slowly to soil applications of humic substances because a large percentage of the humic substances is retained within the roots during plant growth. In most plants less than 30% of the humic substances present within the roots are translocated up the stems into the plant leaves. Foliar applications of relatively small molecular units of humic substances containing trace minerals (on actively growing plants) can be timed to meet the needs of specific plant growth requirements. Applications can be timed to activate vegetative growth, flowering, fruit set, or filling and ripening of fruits.

Side dress applications of commercial liquid humic acids (HAs) and fulvic acids (FAs) to soils during crop production results in direct root uptake. As noted above when humic substances are taken up by plant roots these compounds become concentrated within the roots. Uptake of smaller molecular components of humic substances is both passive and metabolically active. The uptake of high molecular weight humic acids (HAs) by roots is primarily passive; while the uptake of smaller fulvic acids (FAs) polymers is primarily metabolic. After humic acids (HAs) and fulvic acids (FAs) reach a concentration in the root, then a fraction (from 5-30 %) of the total concentration is transported into the shoots and leaves. Radioactive carbon studies indicate that the greatest concentration of humic substances accumulates in plant cell walls and cellular organelles such as the mitochondria and ribosomes. Other similar experiments using radioactive carbon labeled humic acids (HAs) and fulvic acids (FAs) indicates that low molecular weight fulvic acids (FAs) are much more active compared to high molecular weight humic acids (HAs). However some metabolic reactions may require low concentrations of humic acids (HAs) in combination with fulvic acids (FAS). Root growth is primarily stimulated by the molecular components of humic acids (HAs) and fulvic acids (FAS).

Humic acids (HAs) and Fulvic acids (FAS) have direct effects on plant cell membranes. HUMIC acids (HAs) increase the permeability, ease by which mineral elements move back and forth through the cell membranes, resulting in an increased transport of various mineral nutrients to sites of metabolic need. Humic substances influence both hydrophilic (having water affinity) and hydrophobic (lacking water affinity) sites on the membranes surfaces. In addition, many scientists believe that the phospholipid components of the membranes are electrically altered by humic substances. As a result of these electrical changes, the membrane surface becomes more active in the transport of trace minerals from outside the plant cell into the cell cytoplasm.

Energy metabolism is accelerated and the chlorophyll content of plant leaves is enhanced by the presence of humic substances. When Humic Acids (HAs) and fulvic acids (FAS) are applied to plant leaves the chlorophyll content of those leaves increases. As the chlorophyll concentration increases there is a correlated increase in the uptake of oxygen. Chlorophyll development within plant leaves is more pronounced when fulvic acids (FAS) are present in the foliar fertilizer. Organic acids [humic acids (HAs) and fulvic acids (FAS)] also increase the concentration of messenger ribonucleic acids (m-RNA) in plant cells. Messenger RNA is essential for many biochemical processes within cells. Activation of several biochemical processes results in an increase in enzyme synthesis and an increase in the protein contents of the leaves. During these metabolic changes an increase in the concentration of several important enzymes is detected. Some of the enzymes which are reported to increase are: catalases, peroxidases, diphenoloxidase, polyphenoloxidases, and invertase. These enzymes activate the formation of both carrier and structural proteins.

Some molecular components of humic substances act to regulate plant growth hormones. Both humic acids (HAs) and fulvic acids (FAs) inhibit the enzyme, indole acetic acid oxidase (IAA-oxidase), there by hindering IAA destruction. The plant growth regulator, indole acetic acid (IAA) performs many important functions within growing plant parts. When IAA is protected from IAA degrading enzymes the IAA continues to stimulate growth processes. Unfractionated humic acids (HAs) are the most effective in regulating plant growth hormones. Humic substances also influence other enzymes involved in growth regulation. When the activity of growth regulators is maintained within plant tissues, plant metabolism remains functional and normal growth processes continue to occur.

Humic substances increase production of high energy adenosine triphosphate (ATP) within plant cells. As various metabolic systems are activated by humic substances an increase in the production of high energy phosphate bonds (ATP) occurs. The high energy phosphate bonds of ATP function as a major driving energy for many different metabolic reactions.

Humic substances provide many free radicals to plant cells. Free radicals are "active sites" on the polymers which function as electron donors. Free radicals assist in exerting positive effects on seed germination, root initiation and plant growth in general. Free radicals contain one or more unpaired electrons, are highly reactive, short lived, and capable of participating in many different reactions. The free radical content of humic substances is related to the humification state of the humic substance. The greater the humification (low H:C ratios) the darker the color of the humus. Thus humic acids (HAs) contain a higher free radical content compared to fulvic acids (FAS), which have a high H:C ratio. The relatively low free radical content of fulvic acids (FAS), associated with high H:C ratios, is indicative of a low degree of chemical condensation for these substances. Humic acids (HAs) contain two types of free radicals. The first class is a permanent, stable type which persists for longer periods. The second class is a transitional paramagnetic type which is transitory. Each free radical type has a specific function (e.g. catalyst, photo sensitizer, and activators) in various metabolic processes within living cells.

## **SOURCES OF HUMIC SUBSTANCES AND THEIR VALUE AS FERTILIZER INGREDIENTS**

Humic substances commonly occur within soils, waters, peat, and in carbon containing minerals such as brown coals, low grade lignites, and leonardites. Most all soils and waters on the earth surface contain some humic substances in the form of humin, humic acids (HAs), or fulvic acids (FAS). However the concentration of humic substances in agricultural soils has reached seriously low levels. In general soils contain a higher concentration of humin and humic acids (HAs). In contrast, since fulvic acid (FA) is water soluble it occurs at relatively high concentrations in both soils and water. Soil humic substances consist of a higher percentage of ring compounds (aromatic) compared to humic substances from water. Fertilizer grade humic substances can be obtained from carbon containing mineral deposits throughout many parts of the world. Within the United States there are several mines and seams of carbon containing mineral deposits suitable for obtaining good agricultural grade humic substances.

Humic substances can form naturally within soils properly managed. Certain production practices can help build the humus content of soils. Practices such as crop rotation, using balanced fertilization programs, planting legumes, plowing under green manures, returning organic matter to the land, applications of compost, and using minimum tillage practices can all help build humus. Any production practices which damage the activities of living components of the soil should be avoided. Protect the beneficial organisms responsible for forming humus, and they will perform their jobs. Humus building practices are slow, time consuming, and may be costly, however they pay large dividends over time. In order to rapidly return many damaged soils to their former productive capacity growers should consider additional alternatives. An analysis of this situation indicates that the most rapid and practical solution to improving soil fertility is the addition of humates (mined humic substances) directly to the soil or as foliar fertilizers. On most soils the applications of humate based fertilizers is more important than applying traditional N-P-K fertilizers. Humic substances will maximize the efficient use of residual plant nutrients, reduce fertilizer costs, and help release those plant nutrients presently bound in minerals and salts.

Naturally occurring humic substances from low grade lignites and leonardites (nature's soil conditioners), are superior fertilizer ingredients. The best source of humic substances for fertilizer use is from leonardites. Leonardite is defined as a highly oxidized low grade lignite that contains a relatively high concentration of the smaller molecular units (fulvic acids). The smaller humic acids (HA) and fulvic acid (FA) molecules have higher fertilizer value and are readily taken into the plant along with trace minerals. The quality and value of any one mined humate or humic acid product depends on many different factors. A good humic material can be destroyed by improper mining or processing. Thus not all commercially marketed humic substances are equal in quality. It is very difficult for individuals purchasing a humate based fertilizer to tell the difference between a high quality humic substance and a low quality humic material, without laboratory tests. The real test of any humic product is in the field. Growers interested in improving soil fertility and plant health need to set up field tests, with an open mind. Many growers have tried several different commercial humic substance before discovering one that improves crop yields and product quality on their soils. In setting up test plots it is best to establish side-by-side comparisons in the field with a uniform soil type. The whole field should be fertilized as usual and the second half treated with a dry humic substance before planting. In addition liquified humic substance should be applied to the soil and to the foliage as spray during the growing season. In selecting a specific commercial humate product the major concern relates to product quality. Determine if the humate is a blend of humic acids and fulvic acids or is it primarily humic acids. Avoid purchasing pure humic acids. Secondly, does the marketed product have consistency between different batches. An erratically performing product is of minimal value. Another important question is, how rapidly does the product perform in terms of its ability to improve plant growth? One of the best approaches is to ask around and find out which company has quality control procedures in their mining and industrial processing operations. Established companies with experience of working with humates and have a good track record generally market superior humate-based fertilizers.

Quality of humic substances extracted from composts are influenced by the composting ingredients and techniques. Compost starting materials that contain large molecular compounds such as lignins, paraffinic macromolecules, suberins, melanins, cellulose (wood products) and various polyphenols have superior values. In addition to these more complex compost ingredients a blend of compounds containing smaller molecules, such as animal wastes or sludge should also be added to the compost. The length of the composting period, how the compost is turned and watered also influences the quality of compost. A superior compost can be prepared by adding dry Leonardite in with the plant and animal wastes. The added Leonardite creates a more complete balanced of trace mineral elements required by the composting microorganisms. With time the microorganisms and small animals present can synthesize complex humic substances. A large percentage of the currently available plant and animal residues have originated from heavily mined agricultural soils. Many of the by-products of the food industry lack important minerals and vitamins. This fact should be evident from observed vitamin and mineral deficiencies, observed in man and animals. The vitamin and mineral supplement industry is based on the fact that marketed foods and feeds lack certain nutrient requirements. By applying a complete humate based fertilizer or a more complete compost, soil fertility and plant health can be restored.

New standards are needed to monitor the quality of humate based fertilizers currently marketed. The consumer needs

protection from inferior products. There are many “humic acid type” products currently marketed in the United States. Some of these “humic” products have been developed by industrial chemists, industrial concerns have made many attempts to manufacture humic acids using different industrial processes. As a result several “synthetics” have been produced, marketed, purchased, and used. Most of these synthetics have been polymers of vinyl acetate, maleic acid, polyvinyl alcohol, hydrolyzed polyacrylonitrile, carboxymethylcellulose, polyacrilates, isopropyl acrylamide and poly-quaternary ammonium compounds. Generally these synthetic humic molecules have performed poorly in terms of their ability to improve soil fertility or plant growth. These products should not be defined as humate based fertilizer ingredients since their performance under field conditions are very erratic. A chemical analysis of their molecular features reveals that these “synthetics” lack many of the properties of naturally occurring humic substances. They lack the molecular features which improve soil fertility and are frequently incompatible with plant metabolic processes. Other industrial groups have obtained from mature, alkali-insoluble lignite-like coals, treated these materials with degradative and oxidation processes to produce smaller alkali soluble “humic” solutions. The resulting oxidized mixtures from black coals or lignite coals are termed “regenerated humic acids” or “ulmins”. These “ulmins” have characteristics which are similar to humic acids derived from low grade lignites, however are quite different chemically, thus the term “regenerated” is a misnomer. There is no evidence that these “ulmins” have desirable fertilizer grade properties. Hopefully members of the International Humic Substances Society can propose quality standards (labeling) for all commercially marketed humic substances and develop laboratory procedures capable of monitoring the quality of listed ingredients. Until standards can be designed, which are acceptable to the industry, growers and gardeners should purchase humate based (dry and liquid) products that have been extracted from highly oxidized mined low grade lignites or Leonardites. Humic substances from such mineral deposits more closely resemble humic substances normally found in fertile soils and in healthy plants.

Application of humate based dry or liquid fertilizers can improve product quality and increase production. As outlined above humic substances are the building blocks of fertile soils and healthy plants. One important reason for adding humate based fertilizers to the soil is that the producer can again become a steward of the soil. By developing a more ecologically sound agricultural production system it is possible to reduce soil, water, and air pollution. In addition, crop yields will improve and the nutritional value of the harvested products will significantly improve in quality. The extent to which humate based fertilizers improve crop yields depends on the history of cropping practices used on each field. Soils severely damaged by excessive use of acidic fertilizers or pesticides generally respond slowly the first year. Generally the first improvements observed are in product quality. As toxic soil conditions are remediated (corrected) and additional humate-based fertilizers are applied, crop yields and product quality continue to improve.

A word of caution. Avoid applying excess fertilizers (of any type) to soils or plant surfaces. Individuals who apply fertilizers to soils (e.g. producers, farmers, and gardeners) should keep in mind that excessive applications of any fertilizer can create imbalances and even reduce soil fertility. The positive impact of humic substances on plant growth can be reversed by applying excessively high concentrations of these fertilizers. Follow recommendations that have been based on many years of experience.