

Humic Substances in Biological Agriculture

by Lawrence Mayhew

Humankind has realized for thousands of years that dark-colored soils with high humus content are more fertile than light-colored soils. It has long been recognized that humic substances have many beneficial effects on soils and consequently on plant growth. Anywhere on the globe where there is soil or water associated with organic matter, humic substances are present. They cause the brownish tint often seen in natural streams, the darkness of dark soils and the dark brown color of weathered lignite coal.

Humic substances are the most widely distributed organic products of biosynthesis on the face of the earth, exceeding the amount of carbon contained in all living organisms by approximately one order of magnitude (that is, tenfold).

Soil organic matter is defined as the total of all naturally occurring organic (carbon-based) substances found in soils that originate from living things. The process of changing from recognizable bits and pieces of plants (or animals) to an amorphous, “rotted” dark mass is called humification. Humus is defined as the organic matter in soil, a mixture of partially and totally humified substances. Most humic substances result from plant matter subjected to the natural process of decay. Humic substances make up about 80 percent of the soil organic matter in dark soils.

Humic substances in soils are the dark brown, fully decomposed (humified) remains of plant or animal organic matter. They are the most chemically active compounds in soils, with cation and anion exchange capacities far exceeding those of clays. They are long-lasting critical components of natural soil systems, persisting for hundreds or even thousands of years — although they can be destroyed

in less than 50 years by some agricultural practices.

The interest surrounding the use of humic substances arises from the necessity of understanding an essential component of the most complex ecosystem on the globe — soil. The global movement away from chemical to biological agriculture is encouraging some of the best minds in the scientific world to solve the great mystery of how these substances operate in the environment.

As information-age agriculture moves towards biological methods, the world is compelled to reconsider the post-World War II paradigm of indiscriminate use of high-energy input, highly soluble, toxic chemical resources. Natural humic substances are destroyed by conventional practices, but they can be replaced by proper management practices.

Humic substances are the most widely distributed products of biosynthesis on the face of the earth. Besides soils, they can be found in varying concentrations in a number of different sources: rivers, lakes, oceans, compost, sediments, soils, peat bogs and soft coal.

As the use of humic substances in agriculture grows, the number of vendors of humic products is also growing. Historically, the typical supplier has been a small, privately owned operation located where the materials can be easily removed with basic equipment. Because humic substances are typically associated with coal deposits, large coal-mining companies are beginning to realize that the market for these materials can be attractive.

There are a number of theories that attempt to explain how coal is converted

to humic matter. All of them agree that “younger” deposits of organic matter have lower concentrations of humic acid. The concentration of humic substances in converted coal can be as high as 80 percent by weight.

Although humic substances can be found in every scoop of soil and almost every drop of water on the Earth, no one has succeeded in the last 200 years at describing their structure. The chameleon-like humic substances can rapidly rearrange their molecular structure as surrounding conditions change.

The worldwide usage of humic substances is extensive. Their benefits in agricultural soils is well established, especially in soils with low organic matter. They are an integral part of all ecosystems and play an important role in global cycling of nutrients and carbon.

Humic substances are extremely versatile. They provide a concentrated and economical form of organic matter that can replace humus depletion caused by conventional fertilization methods as well as being used in biological programs. The addition of humic substances to soils, including calcareous soils, can stimulate growth beyond the effects of mineral nutrients alone.

HUMIFICATION

Humification is the natural process of changing organic matter such as leaves into humic substances by geo-microbiological mechanisms. Compost is an intermediate product consisting of humic substances and partially decomposed organic matter. As the conversion process continues, different chemicals dominate at different times. Complete conversion to humic substances will eventually occur.

Unlike most other natural biosynthetic processes, humification occurs in a complex, chaotic “open” system where there is no “closed” control of the process by

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Jan-Feb 2004 • Vol. 34, Nos. 1&2

enzymes, cell structures, membranes or cellular transport systems. With the infinite variety of plant materials that exists in nature and with the infinite access to chemical radicals, humification should produce infinitely variable humic substances. It would seem impossible to find two humic molecules with the same structure.

CONFUSION

& NON-STANDARDIZATION

Humic substances have been a matter of scientific controversy for over 200 years. They are incredibly complex colloidal supermixtures that have never been separated into pure components. Inconsistent use of terminology and the previous lack of standard materials for comparison purposes have compromised the ability to translate the sparse amount of scientific knowledge to practical applications in soil environments. Traditionally, humic substances have been defined by their solubility in aqueous (water) solution at arbitrary pH levels and molecular weights.

The use of numerous names to describe commercially available humic materials has contributed to the confusion. Humates, humic acid, leonardite, brown coal, lignite, slack lignite, oxidized lignite, weathered lignite, humalite, fulvic acid, fulvates, ulmic acid, humic shale, carbonaceous shale, colloidal minerals, humin, concentrated humus, soil organic matter, peat, humus acid, humus coal and dead organic matter are some of the terms that are used to describe and/or market humic substances.

Non-standardization and confusion is not limited to humic substances. For example, many labs are using soil tests that may not accurately determine soil organic matter content due to oversimplification. There are numerous tests for soil organic matter, but there is no standardized test protocol for all soils. Some of the tests for soil organic matter have to be interpreted with much caution. Additionally, conventional analyses do not predict possible adverse interactions of trace elements.

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Barley Test

Fertilizer	Tissue Analysis		Plants/row	Yield bu/acere	
	Nitrate ppm	Total N%			
16-20-6	1,275	4.4	68	47.3	
15-22-5	945	4.8	84	47.6	
10-10-5 L	1,025	4.7	96	53.5	

There was a 12 percent increase in yield in the barley test, despite the fact that the leonardite-treated crops had relatively low-nitrate nitrogen. The significant yield advantage was attributed to increased tilling.

Potato Test

Fertilizer	Tissue Analysis		Specific Gravity	Yield	
	Nitrate ppm	Total N%		Cwt.	Bu/acre
16-16-8	820	4.7	1.095	162	270
10-10-5 L	1,600	5.2	1.096	134	224

The potato test plots reveal that a 95 percent increase in plant-tissue uptake of nitrogen was possible even though 35 percent less nitrogen was applied with the leonardite fertilizer combination.

Sugar Beet Test

Fertilizer	Seedling Emergence	Tons/acre	Yield	
			Sucrose%	Sucrose lbs./acre
5-45-5	175	8.873	17.0	3,010
10-10-5 L	140	10.925	15.9	3,474

Sugar beets treated with the fertilizer-leonardite combination yielded 23 percent more tonnage per acre and 15 percent more sugar per acre.

Some scientists have added to the confusion surrounding humic substances by refusing to study the materials, calling them "dirt," thus putting a drag on the flow of scientific knowledge and the study of their beneficial effects on soil and plants.

The establishment of standard reference material by the International Humic Substances Society has helped remedy some of the communication problems. The society is composed of scientists from all over the world who are striving to understand the structures and functions of humic substances.

BENEFITS OF HUMIC SUBSTANCES

While the complete structure of humic substances has eluded scientists, their effects on everything from apples to zucchini have been extensively studied.

Humic substances are renowned for their ability to:

- Chelate soil nutrients
- Improve nutrient uptake, especially phosphorous, sulfur and nitrogen
- Reduce the need for nitrogen fertilization
- Remove toxins from both soils and animals
- Stimulate soil biological activity

- Solubilize minerals
- Improve soil structure
- Act as a storehouse of N, P, S and Zn
- Improve water-holding capacity for better drought resistance and reduction in water usage

Extensive research on the stimulatory effects of humic substances has been conducted by the USDA-ARS soil lab in Minneapolis, Minnesota, and worldwide. Most of the research conducted in Eastern Europe on improving nitrogen utilization has not been translated into English.

Depending on the form of fertilizer applied, nitrogen may become a structural component of humic substances as a stable organic material, preventing it from leaching through the soil. In their natural state, humic substances contain anywhere from 1 to 5 percent nitrogen.

NITROGEN MANAGEMENT

Other effects of humic substances include increased CEC (cation exchange capacity), stabilization of soil structure, and the reduction of nitrogen and phosphorus fertilizers. The importance of humic substances to the fertility of soils and the stabilization of nitrogen has been well documented. One study done by a science team from West Texas A&M University and the USDA-ARS demonstrated the potential of humic substances in reducing ammonia emissions from feed lots.

If there are sufficient humic substances present, up to 35 percent of the soluble nitrogen applied to soils as fertilizer can be retained in the soil in organic forms at the end of the first growing season, thus converting the nitrogen to a stable, bioavailable form.

The ecological impact of nitrogen applied to turf grass is increasingly coming under the scrutiny of the public sector and the federal government. Because of this pressure, humic substances have become the most commonly used organic materials in golf course turf management. After 45 years of research, C. Edward Clapp of the USDA-ARS Department of Soil, Water & Climate in Minneapolis is

recommending the use of humic substances to prevent nitrogen leaching on golf courses.

PELLETIZED LEONARDITE

One of the biggest obstacles to using humic products is the dustiness of the dry materials, making them almost impossible to handle. Liquid humates are easier to handle, but their use is restricted to foliar application at very low concentrations. Because of extremely low application rates, they have no effect on soils. The water-soluble derivatives from alkali extractions are only compatible with high-pH liquids, and they are expensive. Pelletizing humic substances can improve their handling and allow them to be blended with fertilizer “in the row,” where they can do the most good.

A team of scientists with the U.S. Bureau of Mines, University of North Dakota, combined standard NPK fertilizer with leonardite into a pelleted form. Although the addition of leonardite lowered the soluble analysis for NPK to 10-10-5, thus lowering the relative amount of applied fertilizer, the pelleted leonardite combination (10-10-5 L) was effective on barley, potatoes and sugar beets.

Despite the fact that the results concentrated primarily on yield — typical of conventional NPK fertilization programs — the report underscores how humic substances can improve nitrogen utilization and impact overall crop quality by increasing the efficiency of fertilizers (see tables at right). Additionally, the reduction in nitrogen usage demonstrates the environmental significance of using humic substances blended directly with fertilizers.

CARBON CYCLING

The carbon held in soil humic substances is so stable that it can be retained in soils for thousands of years, depending on conditions. The sheer complexity of these materials may explain why they are not broken down more quickly by microbial action. It is possible that the surfaces of humic substances are unrecognizable to microbes.

Conventional fertilizers rapidly age soil components, resulting in acidification of soils and dissolving the humic materials with soluble nitrogen. Urea is so effective at dissolving humic substances that it

is used in some laboratory extraction procedures. A typical Iowa soil under conventional agricultural management retains its carbon for as little as 90 years.

The negative effects of high soil acidity have been extensively researched. Liming, the use of dolomitic limestone (calcium magnesium carbonate), improves soil productivity by providing cations of calcium (Ca²⁺) and magnesium (Mg⁺). The carbonate ions raise the pH by combining with the excessive hydrogen protons.

The ability of humic substances to complex with cations such as calcium is decreased as the bulk pH of soils goes down (that is, as they become more acid) due to aggregation of the humic molecules. The aggregation reduces the exposure of functional groups, cutting off the access of nutrients to the molecules. Functional groups attached to carbon chains are primarily responsible for the biochemical characteristics of organic compounds.

HUMIC ACID, FULVIC ACID & HUMIN

About 200 years ago, the names *humic acid*, *fulvic acid* and *humic* were used to describe what workers believed to be three distinct fractions of humic substances. The three fractions were separated from various materials by using “classical” extraction techniques with aqueous (water) solutions. First, the humic material was treated with a strong alkali (base), then an acid was added. The acid caused a coagulated, black, sludge-like material to precipitate out of solution. They named the precipitate “humic acid.”

The remaining mixture that survived the base/acid treatment consisted of an acidic liquid and a solid. The liquid was named “fulvic acid,” and the solid that was unaffected by the treatments was named “humic.” Despite the fact that manufacturers use variations of these operations, which don’t necessarily duplicate the process described above, the names “humic acid,” “fulvic acid” and “humic” persist.

Potassium hydroxide is the typical alkali used by manufacturers to extract humic acid from leonardite. Since the remaining liquid solution is very alkaline, in the range of 8 to 12 pH, it is incompatible with acids. Here lies some of the confusion, the humic acid synthesized by this operation is not actually an acid. Because

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Jan-Feb 2004 • Vol. 34, No. 1&2

it can also be described as the product of adding acid to an alkaline solution, it is a salt — therefore the word “humate” may be more appropriate.

Some manufacturers follow the traditional method described above by treating the alkaline extract with acid, precipitating out the humic acid portion, leaving behind the so-called fulvic acid fraction in solution. The fulvic fraction is acidic, with a distinctive yellowish tint. Note, however, that the operation is vague. There is no definite pH at which the precipitate and acid are separated.

As various fractions of humic substances are soluble in a wide pH range, it makes sense that some fractions must be soluble at neutral pH. Some manufacturers treat humic materials with water,

Fractation of Humic Substances” that the composition of humin is the same as humic acid and fulvic acid. They say that humin may be a humic substance in association with mineral oxides or hydroxides (from the reaction), or that humin may be coated with hydrocarbons or lipids (fats) stripped during the reaction, making them insoluble to aqueous solvents. Nobody really knows for sure.

Some people think that fulvic acid is more biologically active than humic acid because of its smaller molecular size. There is some truth in these representations as there is evidence that the lower molecular weight fractions have the ability to cross plant membranes and improve permeability of cell walls. It is true that fulvic acids have a higher “total acidity”

tive ingredients become incorporated into the humic complex.

COMPLEX GEOBIOLOGICAL SYSTEMS

The lower molecular weight (the mass of a substance expressed in gram equivalents of its atomic mass) of fulvic acid is sometimes said to account for its greater biological availability. That is somewhat correct, but vague — the industry has not agreed on standardized molecular weights for fulvic acid. Defining humic acid, fulvic acid and humin by their molecular weights is a controversial concept.

Some wet chemistry techniques can be used to characterize different humic materials. For example, the carbon-oxygen ratio is used by some to determine the presence of functional groups. There may be some merit to this, as functional groups are high in oxygen content. The difficulty with wet chemistry techniques is that they rarely mimic the real environments in which these materials are expected to perform.

Humic substances change their structure depending on pH and the type of metals present. High pH (or the presence of multivalent ions, such as calcium Ca^{2+}) makes humic substances open up their long-chain polymers, whereas low pH makes them close. In the presence of toxic metals, humic substances remove the metals from the surrounding environment by forming insoluble aggregated spheres around them.

Humic substances are polymer-like molecules that demonstrate self-organization. The bi-layers formed by humic substances to surround otherwise insoluble minerals are reminiscent of the way all living things utilize biochemical reactions. The self-organized (micellar) colloidal phases act like biological molecules in cellular systems, showing a strong resemblance to the biological mechanisms of living membranes, as described in college textbooks. Humic substances are more like living creatures than chemical entities, but they don't reproduce.

Slight changes in pH will actually cause the humic polymers to fracture, breaking up the original molecules. The fractured molecules are then free to associate with numerous other free radicals, metals or impurities. Humic substances are made up of hundreds of different molecules of many different sizes (polydis-

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extracting the water-soluble fraction, calling that fraction either fulvic acid or “colloidal minerals,” which are promoted in human nutraceutical markets. Fulvic acid can be operationally defined as “the fraction of humic substances that is soluble in water under all pH conditions.”

The marketing of humic substances is interesting in that there is a lack of standardized analysis within the industry for fulvic acid and humic acid. For example, if liquidized humic materials are subjected to analysis, it is difficult to determine what the analysis reveals because of the infinite number of re-associations of free radicals that are possible during the extraction process. Some scientists argue that the reaction products are substances created by alkali treatment as complex degradation products, stripped of many of the original functional groups and recombined into an indescribable material. This may seem to be a nit pick, but some scientists like to argue about it.

The humin fraction gets very little attention. It may seem somewhat inert, but it has been described as acting like a sponge, soaking up nutrients. M.H.B. Hayes and C.L. Graham report in “Procedures for the Isolation and

than humic acids, but the chemical reactivity and chelating ability of humic acids is equal to or greater than fulvic acid, making them very bioactive substances. The humic acid fraction may be more effective than fulvic acid at solubilizing extremely stable aluminum and iron phosphates.

Thirteen carbon nuclear magnetic resonance and mass spectrometric analyses have revealed that the main structural features of humic acid, fulvic acid and humin are nearly identical. To scientists who study humic substances, the names have no meaning chemically. Some scientists say that humic substances from different sources are essentially the same.

Reported variations in plant response to different sources of humic substances are rare. In one case reviewed by Y. Chen and T. Aviad in “Effects of Humic Substances on Plant Growth,” the young age of the humic materials were suspect, because humification is a time-dependent process. As the material ages, more bioac-

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Analysis of Weathered Lignites

Table 1: Geochemical Analysis

Location	SiO ₂ %	Al ₂ O ₃ %	Fe ₂ O ₃ %	MgO %	Na ₂ O %	CaO %	TOT/C %	LOI %	Ash %	Sulfur %	pH	CEC dry basis
North Dakota ^a	6.7	1.8	1.2	1.0	0.42	3.9	44	85	18	2.22	3.8	159
North Dakota ^b	5.3	1.8	0.8	1.0	0.47	6.6	42	80	16	3.27	3.8	111
North Dakota ^c	7.6	2.3	1.3	1.2	0.26	3.4	46	83	13	0.4	4.2	196
North Dakota ^d	3.4	1.4	0.9	1.1	0.31	3.5	51	89	9	0.4	4.2	126
Canada	6.4	2.6	0.5	0.2	0.41	1.6	45	88	36	1.00	3.8	127
Texas	26.9	8.6	1.6	0.4	0.16	0.6	38	60	37	1.00	4.1	78
North Dakota ^e	6.8	3.4	2.5	1.2	0.31	3.4	43	82	15	1.68	3.7	181
New Mexico ^a	17.9	7.9	0.8	0.2	0.26	1.1	32	70	32	0.6	3.5	84
New Mexico ^b	11.9	6.1	0.4	0.1	0.09	0.3	51	80	20	0.5	3.5	72
Utah	24.5	6.0	2.7	0.4	0.22	1.1	41	63	42	2.33	3.6	92

Single analysis, not a database

Table 2: Geochemical Analysis — Contaminants

	Pb ppm	As ppm	Cd ppm	Hg ppb	Se ppm
North Dakota ^a	6	4	0.1	134	6
North Dakota ^b	5	65	0.3	894	1
North Dakota ^c	4	5	0.1	252	3
North Dakota ^d	8	21	0.4	128	2
Canada	6	2	0.1	21	1
Texas	18	1	0.1	80	3
North Dakota ^e	18	1	0.1	128	3
New Mexico ^a	26	2	0.3	58	3
New Mexico ^b	13	1	0.1	0.6	3
Utah	12	3	0.6	0.2	2

Single analysis, not a database

**Table 3:
Humic Acid Analysis**

North Dakota ^a	55%
North Dakota ^b	54%
North Dakota ^c	65%
North Dakota ^d	35%
Canada	70%
North Dakota ^e	70%
New Mexico ^a	57%
New Mexico ^b	30%
Utah	4%

*CDFA Method, dry basis
Single analysis, not a database*

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persity) with many ways to orient themselves by twisting, bending, compressing, and expanding (conformational changes). They are held together loosely by weak forces in a colloidal state.

Any change in solution pH, concentration or the presence of metal ions — especially calcium ions — will cause huge changes in the physical makeup of the humic molecules. Even slight changes cause the molecules to change in orders of magnitude. Rapid changes in molecular structures are not unique to humic substances — water molecules, for example, change their structure 10 trillion times a second. Although water is an extremely simple molecule, the determination of its structure at any given instant is still not fully known. The amazing complexity of humic substances may forever keep their structures a secret.

FULVIC ACID

The primary reason why there is so much confusion about humic substances is the fact that the procedures used to describe them are based on “classical” aqueous extraction. If minerals are present in the parent material, they become complexed by humic substances. This allows more humic and non-humic material to be solubilized during extraction by breaking down ion bridges that would normally hold the molecules together in higher-purity materials. Unless the supernatant is separated by special procedures (such as passing over an XAD-8 resin) to isolate the fulvic portion, the extracted substances may contain amino acids, proteins, sugars or fatty acids in addition to the fulvic acid.

In biological molecules, it is an established fact that the presence of functional groups such as carboxyl, phenol, quinone and hydroxyl are responsible for the activity of these molecules. There is some evidence that there are more functional groups in fulvic than in humic acid. The effectiveness of fulvic extracts may be influenced by the way they are synthesized during chemical processing. The fulvic fraction of humic substances is undoubtedly a beneficial part of oxidized lignites.

IN SEARCH OF A STANDARD

A large percentage of manufacturers are using the services of A&L Western Agricultural Laboratories to determine the quality of their humic substances. A&L Western offers two methodologies for humic substance analysis: the California Department of Food and Agriculture (CDFA) method and the A&L Western method. The CDFA method is a *quantitative* analysis of humic acid. This method reports the acid-insoluble fraction of humic material. The analysis is reported on an “as received” basis (includes moisture). The result can be mathematically converted to a dry-matter basis report.

The CDFA method is based on the operational definition of humic acid. This technique, however, only uses a portion of the methodology described by the International Humic Substances Society method, which analyzes both humic and fulvic acid fractions. The Standard Methods for Soil Analysis of the Soil Science Society of America, as stated by R.S. Swift in “Organic Matter Characterization,” states that the IHSS method is broadly accepted and can be performed in most laboratories. The CDFA method is a compromise, because the fulvic fractions are completely ignored — the fulvic fraction is actually discarded during the process.

The A&L Western method is a *qualitative* analysis, designed to report all of the alkaline-soluble humic materials in a sample. It consistently reports a higher percentage of “humic acid” than the CDFA method. It cannot be converted to a “dry basis.” The A&L Western method may mimic some of the industrial process used to extract humic matter from oxidized lignite. However, the base extraction method cannot discretely remove unwanted materials, nor can it prevent the extracted materials from recombining with free radicals or contaminants. Therefore, the A&L Western method more than likely includes non-humic materials as well as humic substances.

It is important to know the cation exchange capacity (CEC), since these materials are renowned for that characteristic. It should be in the range of 100 to 200 (on a dry-matter basis) as analyzed by the ammonium saturation method. Low pH is very important because the acidity initiates the dissolution of rock minerals.

Low pH may be a broad indicator of open sites for chelating or complexing reactions and an indicator of the relative concentration of functional groups. A pH of about 3.8 is acceptable. An ash content over 10 percent is not unusual, indicating the degree of association with clay minerals or other contaminants. CEC, pH and ash analyses can be performed by many laboratories.

GEOCHEMICAL ANALYSIS

Silicon, iron and aluminum are among the most abundant elements in the Earth's crust and the most common minerals associated with humic substances. Finding a humic substance low in contaminants is challenging, but not impossible. Since humic substances are composed mostly of carbon, a high carbon content can be used as a crude measure. Loss on ignition (LOI) is less reliable, but may be used to confirm the presence of carbon because organic material is burned off during this high-temperature procedure.

Geochemical analysis (Table 1) for total carbon, organic carbon and metal contaminants can be done by an ISO accredited lab, such as Acme Analytical Laboratories, 852 Hastings Street, Vancouver, British Columbia, V6A 1RS, phone (604) 253-3158. The Group 4A and 4B whole-rock geochemical analysis tests for all major elements, 43 trace elements and toxic metals.

Examples of geochemical analysis (Tables 1 and 2) and humic acid analysis (Table 3) of leonardite from nine different mine sites in North America are presented. Aside from the consistent report for pH and sodium, the results demonstrate how there can be variations in CEC, metals, ash, carbon, sulfur, minerals and humic content in various leonardite sources. The report for sodium is intriguing because there are many claims that oxidized lignites of freshwater origin are supposed to be lower in sodium than those derived from ancient sea bottoms.

ENHANCING NUTRIENT BIOAVAILABILITY

Studies of the direct and indirect effects of humic substances on plant growth have repeatedly shown positive effects on plant biomass as long as there is sufficient mineral nutrition. Stimulation

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of root growth is generally more apparent than stimulation of shoot growth.

For many years, the stimulatory effects of humic substances were attributed to hormone-like activity because the action of humic substances was similar to auxins, cytokinins and abscisic acid. This is no longer the case. The stimulatory effects of humic substances have been directly correlated with enhanced uptake of macronutrients, such as nitrogen, phosphorus and sulfur, and micronutrients, such as Fe, Zn, Cu and Mn.

Humic substances enhance the uptake of minerals through the stimulation of microbiological activity. Humic substances actually coat mineral surfaces with a membrane-like bi-layer, which aids in the solubilization of otherwise insoluble compounds by dissolving, complexing, and chelating the dissolved nutrients.

The bioavailability of nutrients released from rock minerals by biological activity is enhanced in the presence of humic substances. Geomicrobiologists have reported that organic acids generated by microbial activity directly influence the rate of dissolution (release of nutrients) from rock minerals.

The implications of this research are astonishing. Whereas conventional farmers are faced with the mandated reduction of soluble fertilizers, sustainable/biological/organic farmers can take advantage of the microbiological release of nutrients from insoluble minerals as the humic substances stabilize and improve the bioavailability of the minerals that are in soil solution.

CALCIUM

Humic substances are becoming renowned throughout the world for their importance in agriculture, especially their ability to chelate nutrient minerals and increase root mass. The benefits to soils and plants are extensive and correlate well with the benefits of humus, organic matter and calcium.

It seems reasonable to conclude that humic substances saturated with unwanted cations and heavy-metal contaminants may lower bioavailability and the efficacy of the product. Therefore, it is important to seek out a high-grade, uncontaminated source. Since there are many sites on a humic molecule for acceptance of cations, it seems reasonable to conclude that calci-

um in combination with humic substances should make a powerful combination.

Many of the benefits of calcium overlap with the benefits of humic substances. Also, the low pH of humic substances along with their biological stimulation and chelating capacity combined with the right dry-calcium source may perform as well as, if not better than, chelated liquid products and calcium chloride. Furthermore, because humic substances are known to complex both cations and anions, creating a synergistic effect, the combined benefits should be greater than the individual ingredients.

In theory, the enhanced benefits should result in increased:

- Biological release of nutrients from otherwise insoluble minerals
- Root growth
- Nutrient uptake from the larger root mass
- Respiration
- Photosynthesis
- Mineral bioavailability and stabilization
- Nitrogen stabilization and fertilizer efficiency
- Disease resistance

Indeed, recent research has demonstrated how the combination of dry calcium with leonardite performed as well as calcium chloride and EDTA, a popular synthetic chelating agent.

HUMIC SUBSTANCES & ROCK PHOSPHATES

The ability of humic substances to solubilize and complex with natural minerals such as rock phosphates is well documented. The bioavailability of nutrients released from rock minerals by microbiological activity is enhanced in the presence of humic substances.

Humic substances can improve the effectiveness of rock phosphates by causing the release of PO_4^{3-} anions and Ca_{2+} cations from hardly soluble rock minerals because of high total acidity and its ability to complex and chelate the resulting solutions and to stimulate microbial metabolism.

Natural leonardite is a complex supermixture of high and low molecular-weight humic substances. The lower molecular-weight constituents (fulvic acids) are primarily responsible for the solubilization of phosphate minerals. Contrary to the typical marketing claims

for "fulvic" acids, the higher molecular-weight components (humic acids) also engage in solubilizing minerals, have a higher capacity for stimulating biological activity, and exhibit greater potential for chelation. In natural soil systems, the two components may act synergistically by complementing each other.

Humic substances also chelate iron, zinc and copper and complex with many other trace elements. Elements typically found in natural phosphate minerals, such as zinc and copper, are known to suppress pathogens and encourage the growth of beneficial organisms.

These phenomena have environmental implications as well because the solubilization of rock phosphates by humic substances can reduce the need for industrial acidification of rock phosphate used for the production of phosphatic fertilizers. Industrial production of phosphate fertilizers is extremely inefficient and creates enormous waste piles that are burdened with contaminants. Additionally, 60 to 80 percent of all highly soluble phosphate fertilizer applied to soils is lost to the environment.

Colloidal humic substances are part of natural soils and help retain nutrients in the soil system through soil stabilization and the stabilization of nitrogen. Furthermore, the complexing action keeps the minerals in solution instead of precipitating (locking up) with soil iron, aluminum and rare earth elements.

APPLYING THEORY TO PRACTICE

Because of their ability to improve fertilizer efficiency, humic substances are best utilized as part of a total fertility program blended into the fertilizer. Programs that include rotations, green manures, cover crops, livestock manure and compost are the best methods to derive the full effect of humic substances. However, the most effective form, dry leonardite, is an extremely dusty material. As discussed in the previous installment, scientists have thus experimented with a pelletized form, and Midwestern Bio-Ag has developed its own pelletized leonardite supplement.

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Research has also confirmed that combining rock phosphate with leonardite can increase the available phosphate analysis from near zero to over 10 percent. Considering that the total P₂O₅ content of the rock phosphate was 20 percent, we can conclude that over 50 percent of the total phosphorus was released from the rock. The released minerals may exist in a chelated form, providing an environmentally safe, bioavailable form of calcium and phosphorus, while avoiding the industrial pollution, energy waste and groundwater contamination created by highly soluble phosphate fertilizers.

SUMMARY

Humic substances are formed by a process called humification. The humification process is chaotic, with innumerable reactions occurring under countless conditions. The process occurs over geological time, therefore younger deposits of humic materials generally have lower concentrations of humic acid.

Humic substances are critical components of water and soil ecosystems, which are essential to soil genesis and the global cycling of carbon and nutrients. The interactions among microbes, clays and minerals are dependent upon humic substances. The vast agronomic and environmental importance of these materials is just beginning to be appreciated.

Distinctions based on molecular mass (weight) or the quantity of functional groups and fulvic acid content seem useless if there is no agreement regarding the methods used to evaluate the materials. The quality of natural humic materials can be assessed by pH, CEC, total carbon, total organic carbon, and association with calcium, silicon, sulfur, iron, aluminum and toxic contaminants. The concentration of humic acid and fulvic acid can be analyzed by some labs since standard reference materials and procedures for the extraction and analysis of humic substances are available from the International Humic Substances Society.

The agronomic effectiveness of humic materials may be influenced by the presence of metals associated with the natural

ores. Because humic substances are powerful complexing and chelating entities, association with silicon, aluminum or iron (typically found in clays) may influence the materials in soil systems. Research based on the agronomic effectiveness of humic materials (oxidized lignites) from different sources has not been performed.

CONCLUSION

The conventional tools of chemistry have not been able to explain why these materials work in complex soil ecosystems. They have all the qualities of humus in a compact convenient package. Although examination of the microscopic detail and structure of humic substances is currently not achievable, their beneficial properties are evident. The ecological and plant-nutritional benefits provide sufficient justification for using these extraordinarily complex eco-minerals.

If the supply side of the industry so chooses, a set of standards could be adopted by a professional society or trade group representing the industry. An independent laboratory could monitor the standards. Some of the best and brightest professionals in the industry are working toward that goal.

Standardization of materials may also provide a basis for acceptance by state fertilizer regulators. Anyone in the supply industry should seriously consider joining the International Humic Substances Society to communicate the industry's needs to the scientific community. Besides, scientists need to be reminded sometimes that there are many good people who can benefit from their knowledge. That knowledge needs to be communicated to everyone, not just other scientists.

For the consumer, there is an endless variety of applications for humic substances, both as agronomic inputs and as human health aids. Humic substances are part of an environmental engineer's toolbox for the bioremediation of toxic contaminants. Humic substances are possibly the most versatile natural substances ever known.

More information on humates, including citations for the scientific literature discussed in this study, is available by request from Midwestern Bio-Ag, phone 1-800-327-6012, or by accessing their website at <midwesternbioag.com>.

Richard Lamar has a great deal of experience analyzing oxidized lignites. He is currently with EarthFax, a soil reclamation, civil, geotechnical and environmental engineering firm, where his lab is set up to analyze humic substance using techniques that follow the IHSS protocols. EarthFax can be reached at 1770 North Research Park Way, North Logan, Utah 84341, phone (435) 787-2743, e-mail <rlamar@pcu.net>, website <www.earthfax.com>. R.S. Swift's "Organic Matter Characterization" is included in Methods of Soil Analysis, Part 3: Chemical Methods, available from the Soil Science Society of America, phone (608) 273-8080, fax (608) 273-2021, website <www.soils.org>.

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