

Humic Substances in Biological Agricultural Systems

Introduction

by Gary Zimmer

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Organic matter, compost, humus, humates, humic acid, and fulvic acid are all related to, and parts of, decaying plant materials. It's food for soil life and a storehouse for minerals, energy and water. These organic materials are mediums for certain organisms to grow on. The biological/organic farming system is based on balanced minerals and lots of soil life in terms of diversity and volume.

So where do humic substances fit in farming systems? The objective of this article is to clarify some of the confusion about humic substances, update and review the scientific research and provide guidelines for use of the many different humic materials being marketed.

Research is proving what farmers have long known to be true: humic substances stimulate plant roots, stimulate soil life (mostly fungal populations), chelate minerals (holding them for future use by plants), improve absorption of minerals for root and plant use, and improve the effectiveness of herbicides.

In the first section of this paper I'll explain the different humic products available and how they presently are being used. The last section is a scientific review completed by Lawrence Mayhew, working in Product Development for Midwestern Bio-Ag.

Humates

Humate is a common term used to describe dry mined carbonaceous materials found in areas where coal is mined. They are correctly called Leonardites or oxidized Lignites. For many years the most commonly used humic product was a black liquid extract called humic acid. Humic acid is obtained by mixing a strong base liquid material like sodium hydroxide or more commonly potassium hydroxide with a dry humate material. The black humic acid material (not really an acid because of the base extraction has a pH of 9+), usually a 6% or 12% solution, was most commonly mixed with fertilizers, used in transplant solutions mixed with liquid nitrogen sources or mixed with herbicides. Because of its high pH you had to be careful because it would cause the liquid mix to jell, or precipitate out. Mixing it with phosphorus materials was a real problem in many situations.

Besides, mixing it in transplant solutions (where it is highly diluted and didn't give many problems) my favorite place to use humic acid is mixing it with liquid nitrogen sources. It gives an organic material for the nitrogen to hook to, therefore reducing the leaching and loss of nitrogen and buffering the solution for more effective and efficient use. A rate of 1-3 gallons/acre, depending on nitrogen needs (which can be reduced with humic acid use) seems to work best from my observations.

Fulvic acid, another extraction from the dry humates, is truly an acid. It is an acid extraction and has a pH near 3.0. It can be mixed with any liquid compound without difficulty. It is a part of the original material but quite different from the humic acid. My favorite place to use it is in liquid fertilizer mixes to buffer the soluble fertilizer, chelate it and improve its uptake by the plants. Another area of common use is mixed with herbicides, besides acidifying the tank mix which helps the effectiveness of the herbicide, it again also chelates and improves the intake of the chemical. Application rates are from one quart to one gallon/acre, depending on the crop, and on the amount and type of fertilizer and chemicals used.

Now if you have extracted part of the original humic substance (humic acid) with a base, then another part (fulvic acid) with acid, what you have left is a large molecule called humin, the 'sponge' as it is known because it holds and absorbs things.

My belief in agriculture is that, where ever possible, don't take parts or pieces, but use the whole compound. Sometimes the parts we leave behind have some real benefits like the calcium, trace elements and rare earths remaining when the fertilizer industry extracts phosphorus from rock phosphates. The same is true for the minerals, vitamins, hormones and other unknown compounds left behind when cytokinins are extracted from kelp. Where ever possible, why not use the whole?

As for humic substances, in the last few years micronized compounds with added suspending agents have been showing up in the marketplace. This is the original humic material ground really fine. It's an expensive process and not fool proof, as precipitation of materials and spray nozzle plugging has occurred, but the idea makes sense. This material can be used anywhere humic and fulvic acids are used. Not being the same as them because of the base or acid treatment, but having the same materials in them.

In my biological farming experience, after a lot of observations and testing, dry fertilizer mixes give more flexibility and are better buys. Plus, you can balance the soluble to slow release materials. Liquid fertilizers are water soluble, can leach, tie up in the soil, cause short term nutrient imbalances, and don't provide nutrients over the plant's life. They have their place as a pop-up to get the crop out of the ground or as a foliar to give a boost, but not as a complete fertilizer program.

So humic substances and dry fertilizers, how can they work together? I've tried bulk spreading dry humates on soils. They're dusty, hard to handle and I struggled to find any measurable results.

It makes sense to add humic substances to fertilizer materials to provide carbon, a buffering, chelating agent, and some microbe foods. Using the original raw material is providing the most benefits for the dollar. Yet, handling that black dusty humic material seemed unworkable for most fertilizer blenders.

In Australia, farmers and consultants are blending humates with natural phosphates, calcium, sulfur and trace mineral materials, inoculates with beneficial organisms, adding molasses, and brewing the batch: just like making compost. The natural humic material has a low pH, large nutrient holding capacity and feeds microbes. The results looked good and the process makes sense.

However, the problem is still handling. You certainly can't put it down the row as a crop fertilizer. The secret to fertilizing is a balance of nutrients, the concentration putting them where and when needed and the recovery throughout the growing season.

Pelletizing

To overcome these problems, we at Midwestern Bio-Ag started pelletizing the humic materials, and mixing them with calcium sources and rock phosphates.. It's not an easy process and because of the nature of the material, it's hard to keep it in a hard pellet form.

During early attempts, something surprising occurred. When a pile of humic substances is pre-mixed with rock phosphates and allowed to sit for a period of time, the measurable soluble phosphorus content went up! A reaction occurred; the moist low pH humic materials released activating the rock phosphate (the same thing that was happening in the brew piles in Australia). The beneficial results in the field have really been noticeable!

Humic materials from my experiences belong mixed with fertilizers. Not only can humic materials buffer fertilizers, but also chelate, holding nutrients for longer plant use.

Our next step in pairing humic materials with buffers is to make up homogenized trace mineral mixes using sulfate trace minerals paired with humic substances. This should also chelate the mineral for more efficient and long term use.

In our effort to help farmers, consultants, and agricultural researchers to better understand humic substances, Lawrence Mayhew, Midwestern Bio-Ag's product development specialist, did an extensive review of current scientific research about the material. Research gives us clues and ideas in this field of agriculture, then we need to evaluate this research as to where it fits and how it can be best utilized.

The updated scientific study that follows will, I hope, give you a better understanding and clarification of what humic substances are, and are not, and what researchers have seen and measured.

Humic Substances as Agronomic Inputs in Biological Agricultural Systems: a Review

by Lawrence Mayhew

Background

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 (Muller-Wegener, 1988). Anywhere on the globe where there is soil or water associated with organic matter, humic substances are present. They are 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 (Tan, 2003), exceeding the amount of carbon contained in all living organisms by approximately one order of magnitude (Steinberg, 2003).

Soil organic matter is defined as the total of all naturally occurring organic (carbon based) substances that are found in soils, which have come 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 that is a mixture of partially and totally humified substances. Most humic substances come from the natural process of decaying plant matter. (Hayes, 1998) Humic substances make up about 80% of the soil organic matter in dark soils. (Schnitzer, 1986)

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 (Tan, 2003) with cation and anion exchange capacities far exceeding clays. They are long lasting critical components of natural soil systems, persisting for hundreds to thousands of years, which can be destroyed in less than fifty years by some agricultural practices.

The interest surrounding the use of humic substances comes forth from the necessity to understand an essential component of the most complex ecosystem on the globe...soils! 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, high solubility, and toxic chemical resources. (Nardi, et al, 1996) Natural humic substances are destroyed by conventional practices, but can be replaced by proper management practices.

Humic substances are the most widely distributed products of biosynthesis on the face of the earth (Tan, 2003). 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 may 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 (Tan, 2003). The concentration of humic substances in the converted coal can be as high as 80% 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. (Steelink, 1999) Behaving more like chameleons, humic substances rapidly rearrange their molecular structure as the surrounding conditions change (Tombacz and Rice, 1999).

The worldwide usage of humic substances is extensive (Fataftah, et al, 2001) The benefits of humic substances in agricultural soils is well established (MacCarthy, 2003), especially in soils with low

organic matter. (Chen and Aviad, 1990) They are an integral part of all ecosystems and play an important role in global cycling of nutrients and carbon (MacCarthy, 2003).

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. (Burdick, 1965) The addition of humic substances to soils, including calcareous soils, can stimulate growth beyond the effects of mineral nutrients alone. (Chen, et al, 1999)

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 points in time (Ziechmann, et al, 2000). 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 enzymes, cell structures, membranes or cellular transport systems. With the infinite variety of plant materials that exist in nature and with the infinite access to chemical radicals, humification should produce humic substances that are infinitely variable. (Ziechmann, et al, 2000) It would seem impossible to find two humic molecules with the same structure.

Confusion and Non-Standardization

Humic substances have been a matter of scientific controversy for over 200 years. They are incredibly complex colloidal supermixtures (MacCarthy, 2001) that have never been separated into pure components. (Steelink, 1999; MacCarthy, 2001) 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 (Tabatabai, 1996), 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 (Magdoff, 1996). Additionally, conventional analyses do not predict possible adverse interactions of trace elements (Olness et al, 2002).

In the past, some scientists have added to the confusion surrounding humic substances by refusing to study the materials, calling them “dirt” (Tan, 2003), thus putting a drag on the flow of scientific knowledge and the study of their beneficial effects on soil and plants (Stevenson, 1994).

The establishment of standard reference material by the International Humic Substances Society <http://www.ihss.gatech.edu/> has helped to 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. The north-central United States contact is Dr. Alan E. Olness, USDA-ARS, North Central Soil Conservation Research Laboratory, Morris, MN 56267, 320-589-3411 x131.

The 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 (Frank and Roeth, 1996)
- improve water holding capacity for better drought resistance and reduction in water usage (Russo and Berlyn, 1990),

Extensive research on the stimulatory effects of humic substances has been conducted by the USDA-ARS soil lab in Minneapolis (Clapp et al, 2001; Chen et al, 2001; Chen et al, 1999) and worldwide (Karr, 2001). Most of the research conducted in Eastern Europe on improving nitrogen utilization has not been translated into English (Clapp et al, 2001).

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. (Haworth, 1971; Stevenson, 1982; Haynes and Swift, 1990; Kelly and Stevenson, 1996) In their natural state, humic substances contain anywhere from 1% to 5% nitrogen.

Despite the fact that all humic substances possess the abilities described above, regardless of their origin or molecular weight (Wershaw, 2000; MacCarthy, 2001, p.24), many vendors of humic substances engage in a bit of “chest beating” when making claims about their products based on arbitrary definitions of “humic acid” and “fulvic acid” content. (Fataftah, et al, 2001)

Nitrogen Management

Other effects of humic substances include increased CEC (cation exchange capacity), stabilization of soil structure (Piccolo et al, 1999) and the reduction of nitrogen and phosphorus fertilizers. (Day, et al, 2000; Fataftah, et al, 2001) The importance of humic substances on the fertility of soils and the stabilization of nitrogen has been well documented (Thorn, 2000; Kelly and Stevenson, 1996; Nardi, et al, 1996). One study done by a science team from West Texas A&M University and the USDA-ARS (Shi et al, 2001) demonstrated the potential of humic substances in reducing ammonia emissions from feed lots.

If there are sufficient humic substances present, up to 35% of the soluble nitrogen applied to soils as fertilizers can be retained in the soil in organic forms at the end of the first growing season (Stevenson and Xin-Tao He, 1990), thus converting the N to a stable, yet 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 (Clapp et al, 1998). After 45 years of research, C. Edward Clapp of the USDA-ARS, Department of Soil, Water & Climate in Minneapolis, Minnesota is recommending humic substances be used to prevent nitrogen leaching on golf courses (Clapp, 2001).

An exhaustive review of the scientific literature has revealed very little regarding the practical application of humic substances in agriculture. There are numerous references to a large body of research in Russia that has not been translated into English. A recent reference (Steinberg, 2003) states that most of the information is buried as internal reports within universities.

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 improves their handling and allows them to be blended with fertilizer “in the row” where they can do the most good.

A team of scientists with the US Bureau of Mines, University of North Dakota combined standard NPK fertilizer with Leonardite into a pelleted form (Cooley et al, 1967). Although the addition of Leonardite lowered the soluble analysis for N, P, & K 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.

Barley Test

Fertilizer	Tissue Analysis		Plants / row	Yield bu / acere
	Nitrate ppm	Total N %		
16-20-6	1275	4.4	68	47.3
15-22-5	945	4.8	84	47.6
10-10-5 L	1025	4.7	96	53.5

There was over a 12% increase in yield in the barley test a plot despite the fact that the Leonardite treated crops had relatively low nitrate nitrogen. The significant yield advantage was attributed to increase tillering.

Potato Test

Fertilizer	Tissue Analysis		Specific Gravity	Yield	
	Nitrate ppm	Total N %		C Wt.	Bu/acre
16-16-8	820	4.7	1.095	162	270
10-10-5 L	1600	5.2	1.096	134	224

The potato tests plots reveal how a 95% increase in plant tissue uptake of nitrogen was possible while 35% less nitrogen was applied with the Leonardite fertilizer combination.

Sugar Beet Test

Fertilizer	Seedling Emergence	Yield		
		Tons / acre	Sucrose %	Sucrose lbs. / acre
5-45-5	175	8.873	17.0	3010
10-10-5 L	140	10.925	15.9	3474

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

Despite the fact that the above report from the US Bureau of Mines concentrated primarily on yield, which is 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. 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 it may be retained in soils for thousands of years, depending on conditions. (Miller and Gardiner, 1998) The sheer complexity of these materials may explain why they are not broken down by microbial action for thousands of years. (Schnitzer and Khan, 1972) It is possible that the surfaces of humic substances are unrecognizable by microbes. (Orlov et al, 1994).

Conventional fertilizers rapidly age soil components, resulting in acidification of soils (Burdick, 1965; Barak, 1999) and by dissolving the humic materials with soluble nitrogen. Urea is so effective at dissolving humic substances, it is used in some laboratory extraction procedures. (Pokorna et al, 1999) A typical Iowa soil under conventional agricultural management retains its carbon for as little as 90 years. (Miller and Gardiner, 1998)

The negative effects of high soil acidity have been extensively researched. "Liming", which is the use of dolomitic limestone (calcium magnesium carbonate) improves soil productivity by providing cations of calcium (Ca^{2+}) 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 (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. (Liu and Huang, 1999) Functional groups attached to carbon chains are primarily responsible for the biochemical characteristics of organic compounds.

Humic Acid, Fulvic Acid and Humin

The traditionally accepted definition of humic acid, fulvic acid and humin is much like defining common table salt as "the remaining solids left over from the evaporation of seawater". One would say that the remaining material after evaporation is **operationally defined** instead of calling it what it really is; sea salt, a mixture of numerous minerals along with sodium chloride. Common table salt, by the way, contains sodium chloride along with other chemical additives, such as sodium aluminosilicate, to help it flow out of a salt shaker.

About 200 years ago, the names humic acid, fulvic acid and humin 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. (Schnitzer, 1999) 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 which was unaffected by the treatments was named "humin". 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 humin 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, "humic acid" synthesized by this operation is not an acid. Because 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, extracting the water-soluble fraction, calling that fraction either fulvic acid or "colloidal minerals", which are promoted in the human nutraceutical markets. Fulvic acid can be operationally defined as "the fraction of humic substances that is soluble in water under all pH conditions (MacCarthy, 2003). Humic Acid, Fulvic Acid and Marketing

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 (Pokorna et al, 2001). 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 to be somewhat inert but it has been described as acting like a sponge, soaking up nutrients (Karr, 2002). Hayes and Graham (2000) report the composition of humin to be 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). Alternatively, humin

may be coated with hydrocarbons or lipids (fats) that were 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" than humic acids (Tan, 1986), however the chemical reactivity and chelating ability of humic acids is equal to or greater than fulvic acid (Tan, 2003) making them very bioactive substances. The humic acid fraction may be more effective than fulvic acid at solubilizing extremely stable aluminum and iron phosphates (Lobartini et al, 1998).

¹³Carbon 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 (Wershaw, 2000; Schnitzer, 1999). Some scientists say that humic substances from different sources are essentially the same. (Pokorna et al, 1999; Cook and Langford, 1999; Gajdosova, 2000)

Reported variations in plant response to different sources of humic substances are rare. In one case reviewed by Chen and Aviad (1990), the young age of the humic materials were suspect, because humification is a time dependant process. As the material ages, more bioactive ingredients become incorporated into the humic complex (Ziechmann et al, 2000). Old age is good.

Wet Chemistry vs. 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 (Chen and Aviad, 1990), but very vague because 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 it rarely mimics the real environment in which these materials are expected to perform.

Humic substances change their structure depending on pH and the type of metals present. (Kolla, 1998; Piccolo et al, 2000) High pH (or the presence of multivalent ions, such as calcium Ca^{2+}) makes humic substances open up their long chain polymers and 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 (Liu and Huang, 1999).

Humic substances are "polymer-like" molecules that demonstrate self-organization. (Hayes, 1998; Cook and Langford, 1999; Piccolo, et al, 2000) The bi-layers formed by humic substances to surround otherwise insoluble minerals (Tombacz and Rice, 1999) are reminiscent of the way all living things utilize biochemical reactions to carry on life in general. The self-organized (micellular) colloidal phases act like biological molecules in cellular systems, showing a strong resemblance to the biological mechanisms of living membranes, as described in college text books, such as Voet and Voet, 1995. 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. (Tombacz and Rice, 1999, Piccolo, et al, 2000) 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 (polydispersity) with many ways to orient themselves by twisting, bending, compressing and expanding (conformational changes). They are held together very loosely by weak forces (Piccolo, et al, 2000) 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 make up of the humic molecules. Even slight changes cause the molecules to change in orders of magnitude (Tombacz and Rice, 1999). Rapid changes in molecular structures are not peculiar to just humic substances. Water molecules change their structure 10,000,000,000,000 times a second. (Voet and Voet, 1995) Although water is an extremely simple molecule, the determination of its structure at any given instant is still somewhat unknown. 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 some 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 (Ozdoba, et al, 2001) 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 a XAD-8 resin) to isolate the fulvic portion, the extracted substances may contain anything from amino acids, proteins, sugars or fatty acids in addition to the fulvic acid (Hayes and Graham, 2000).

In biological molecules, it is an established fact that the presence of functional groups, such as carboxyl, phenol, quinone and hydroxyl groups are responsible for the activity of these molecules. There is some evidence that there are more functional groups in fulvic than 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.

Analysis of Humic Substances: In Search of a Standard

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 for open sites for chelating or complexing reactions to take place and an indicator of the relative concentration of functional groups. A pH of about 3.8 is acceptable. An ash content over 10% is not unusual, indicating the degree of association with clay minerals or other contaminants (Ozdoba, et al, 2001). CEC, pH and ash analysis can be performed by many laboratories.

A large percentage of manufacturers are using the services of A&L Western Agricultural Laboratories, Inc. to determine the quality of their humic substances. A&L offers two methodologies for humic substance analysis; the California Department of Food and Agriculture method (CDFA) 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 (IHSS) method, which analyzes both humic acid and fulvic acid fractions. The *Standard Methods for Soil Analysis of the Soil Science Society of America, Madison, Wisconsin* (Swift, 1996) states that the IHSS method is broadly accepted and it 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, which may 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 Method more than likely includes non-humic materials as well as humic substances.

One person who has some experience analyzing oxidized lignites is Richard Lamar of EarthFax Engineering, Midvale, UT 84047, (435-787-2743), a soil reclamation, civil, geotechnical and environmental engineering firm, just to name a few. His lab is set up to analyze humic substances using techniques that are similar the IHSS protocols. It's a bit pricey, but Richard says he can get the price down in the future if there are sufficient requests for the service. He seems to understand the industry.

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. (Liu and Huang, 2000) 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.

Geo-chemical 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 includes all major elements, 43 trace elements and toxic metals.

Examples of geochemical analysis (Tables 1 and 2) and humic acid analysis (Table 3) of oxidized lignite, Leonardite and humic shale 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 the various sources. The report for sodium is intriguing because there are many claims that oxidized lignites of fresh water origin are supposed to be lower in sodium than those derived from ancient sea bottoms.

Humic Substances Enhance 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 of root growth is generally more apparent than stimulation of shoot growth. (Chen and Aviad, 1990; Nardi, et al, 1996; Abad et al, 1991)

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 (Clapp et al, 2001). The stimulatory effects of humic substances have been directly correlated with enhanced uptake of macronutrients, such as nitrogen, phosphorus, sulfur (Chen and Aviad, 1990) and micronutrients, i.e. Fe, Zn, Cu and Mn. (Chen et al, 1999).

Humic substances enhance the uptake of minerals through the stimulation of microbiological activity. (Albuzio et al, 1994; Figliolia et al, 1994; Visser, 1995; Nardi, et al, 1996; Paciolla, et al, 1998; Day et al, 2000) Humic substances actually coat mineral surfaces with a membrane-like bi-layer, which aids in the solubilization of otherwise insoluble compounds (Tombacz and Rice,, 1999) 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. (Chen and Aviad, 1990) Geo-microbiologists have reported that organic acids generated by microbial activity directly influence the rate of dissolution (release of nutrients) from rock minerals (Barker et al, 1997; Welch et al, 2002).

The implications of this research are astonishing. While conventional farmers are faced with the mandated reduction of soluble fertilizers, sustainable, biological and organic farmers can take advantage of the microbiological release of nutrients from insoluble minerals while 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 (Fataftah, et al, 200; Tan, 2003), especially their ability to chelate nutrient minerals (Chen et al, 2001) and increase root mass (Amarasiriwardena et al, 2000; MacCarthy, et al, 1990; Chen and Aviad, 1990). 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 must be important to seek out a high grade uncontaminated source. Since there are many sites on a humic molecule for acceptance of cations (Tan, 1986), it seems reasonable that calcium 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 (Tan, 2003). Furthermore, because humic substances are known to complex both cations and anions (Huang and Violante, 1986; Mortland, 1986) creating a synergistic effect (Clapp et al, 2001), the combined benefits should be greater than the individual ingredients.

In theory, the enhanced benefits should result in greater:

- biological release of nutrients from otherwise insoluble minerals (Tan, 1986; Chen and Aviad, 1990; Banfield and Hamers, 1997; Barker et al, 1997)
- root growth, (Chen and Aviad, 1990, Chen et al, 2001)
- nutrient uptake from the larger root mass (Kapulnik, 1996)
- respiration (Nardi, et al, 1996; Marschner; 1999, Chen et al, 2001)
- photosynthesis (Marschner, 1999, Chen et al, 2001)
- mineral bioavailability and stabilization (Banfield and Hamers, 1997)
- nitrogen stabilization and fertilizer efficiency (Fenn, et al, 1995; Clapp, 2001)
- disease resistance (Marschner, 1999)

Indeed, recent research has demonstrated how the combination of dry calcium with oxidize lignite performed as well as calcium chloride and EDTA, a popular synthetic chelating agent. (Pare', et al, 2001)

The Effect of Humic Substances on Rock Phosphates

The ability of humic substances to solubilize and complex with natural minerals, such as rock phosphates, is well documented (Chen, et al, 1999; Burdick, 1965; Banfield and Hamers, 1997; Schnitzer, 1986; Martinez et al, 1984; Tan, 1986). The bioavailability of nutrients released from rock minerals by microbiological activity is enhanced in the presence of humic substances (Chen and Aviad, 1990).

Humic substances can improve the effectiveness of rock phosphates by causing the release of $(\text{PO}_4)^{3-}$ anions and $(\text{Ca})^{2+}$ cations from hardly-soluble rock minerals (Sinha, 1971; Lobartini et al, 1994) because of high total acidity (Tan, 1986), ability to complex and chelate the resulting solutions (Tan, 1986; Chen, et al, 1999; Clapp, et al, 1999) and stimulate microbial metabolism (Albuzio et al, 1994; Figliolia et al, 1994; Nardi, et al, 1996; Paciolla, et al, 1998; Day et al, 2000; Chen et al, 1999; Visser, 1985).

Natural Leonardite or oxidized lignite 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 (Levesque and Schnitzer, 1967; Weir and Soper, 1963). Just like the fulvic acid fractions, the higher molecular weight components (humic acids) also engage in solubilizing minerals, have a high capacity for stimulating biological activity and greater potential for chelation (Tan, 2003). In natural soil systems, the two components may act synergistically by complementing each other.

Humic substances also chelate iron, zinc, copper and complex with many other trace elements (Clapp, 2001). Elements typically found in natural phosphate minerals, such as zinc and copper, are known to suppress pathogens and encourage the growth of beneficial organisms (Duffy and Defago, 1999).

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% of all highly soluble phosphate fertilizer applied to soils is lost to the environment (Griffin et al, 2003).

Colloidal humic substances are part of natural soils and help retain nutrients in the soil system through soil stabilization (Piccolo et al, 1999) and the stabilization of nitrogen (Day, et al, 2000). Furthermore, the complexing action keeps the minerals in solution instead of precipitating (locking up) with soil iron, aluminum (Tan, 1986; Banfield and Hamers, 1997; Schnitzer, 1986) and rare earth elements (Banfield and Hamers, 1997).

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 or oxidized lignite, is an extremely dusty material.

In order to improve the handling of the dusty material and to take advantage of the benefits derived from whole, natural material, Midwestern Bio-Ag has succeeded in pelletizing Leonardite with various combinations of calcium products. The results of field trials conducted by customers are consistent with the reports in the scientific literature of the effectiveness of blended products.

The release of nutrients from insoluble minerals has been confirmed also. By combining rock phosphate with Leonardite (oxidized lignite), the available phosphate analysis (AOAC, 1999) can increase from near zero to over 10%. When considering that the total P_2O_5 content of the rock phosphate was 20%, that means that over 50% 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 ground water contamination created by highly soluble phosphate fertilizers.

Summary and Discussion

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.

Distinction based on molecular mass (weight) or the quantity of functional groups and fulvic acid content are 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 because 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 cannot be applied to these materials to explain why they work in complex soil ecosystems. They have all the qualities of humus in a compact convenient package. Although 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 some kind of 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 (IHSS) 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 bio-remediation of toxic contaminants. Humic substances are possibly the most versatile natural substances ever known.

Analysis of Weathered Lignites

Table 1

Geochemical Analysis												
Location	SiO2	Al2O3	Fe2O3	MgO	Na2O	CaO	TOT/ C	LOI	Ash	Sulfur	pH	CEC
	%	%	%	%	%	%	%	%	%	%		dry basis
North Dakota	6.7	1.8	1.2	1.0	0.42	3.9	44	85	18	2.22	3.8	159
North Dakota	5.3	1.8	0.8	1.0	0.47	6.6	42	80	16	3.27	3.8	111
North Dakota	7.6	2.3	1.3	1.2	0.26	3.4	46	83	13	0.4	4.2	196
North Dakota	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	6.8	3.4	2.5	1.2	0.31	3.4	43	82	15	1.68	3.7	181
New Mexico	17.9	7.9	0.8	0.2	0.26	1.1	32	70	32	0.6	3.5	84
New Mexico	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

Contaminants					
	Pb	As	Cd	Hg	Se
	ppm	ppm	ppm	ppb	ppm
North Dakota	6	4	0.1	134	6
North Dakota	5	65	0.3	894	1
North Dakota	4	5	0.1	252	3
North Dakota	8	21	0.4	128	2
Canada	6	2	0.1	21	1
Texas	18	1	0.1	80	3
North Dakota	18	1	0.1	128	3
New Mexico	26	2	0.3	58	3
New Mexico	13	1	0.1	0.6	3
Utah	12	3	0.6	0.2	2
Single analysis, not a database					

Table 3

Humic Acid	
North Dakota	55%
North Dakota	54%
North Dakota	65%
North Dakota	35%
Canada	70%
North Dakota	70%
New Mexico	57%
New Mexico	30%
Utah	4%
CDFA Method, dry basis	
Single analysis, not a database	

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