Humic Acids

A Practical Look

There are hundreds of published papers, technical write ups and books on the subject of humic acids, many of which may be essential for the scientists understanding, but most of which do not hold practical value for someone who wishes to use humic acid in a fertility program. The purpose of this Bio-Gro CFS information sheet is to look at the most important subjects of humic acids in practical terms. Our hope is that this information sheet will be informative for fertility experts and growers alike.

A Brief Introduction

Research on the subject dates back more than 200 years, when in the 1760's a scientist made the observation that humic substances adsorbed water and plant nutrients.1 Oddly, in the 21st century, the commercially represented definition of "humic acids" as not evolved much past the observations of a scientist named Mulder,1 who, in the 1840's subdivided humic substances into three groups:

1) Materials that were insoluble in alkali were referred to as ulmin and humin.
2) Materials that were soluble in alkali were classified as ulmic when brown and humic when black.
3) Materials soluble in water were referred to as crenic or apocrenic acids.

Later between 1912 and 1919, Oden proposed that crenic and apocrenic acids be referred to as fulvic acid. Oden made many other observations, including that humic substances contained carboxyl and phenolic hydroxyl groups.2

Since that time there have been volumes of research papers and technical manuals published on the subject. The majority of the attention is directed towards classifying and thoroughly understanding the chemical make up and formation processes of humic substances.

From this information, we at Bio-Gro, Inc., have focused on the chemical properties of humic acids, specifically those comparing humic acids from different sources such as; water, soils, compost, peat and lignite. We have also gathered information to help us better understand which fractions of humic acids are most "bio-active". This work has resulted in important breakthroughs in our extraction methods used in the production of our commercial humates.

What are humic & fulvic acids?

Generally, humic acids are a product of decomposition of organic matter (composting is one type of decomposition). Overburdens to coal beds (lignite or leonardite) are an ancient form of "compost" that has a lot of concentrated humic acids. Technically, the term "humic acids" refer to the portion of decomposed organic matter that is soluble in a base (alkaline – high pH) solution. To summarize:

Fulvic acid	The fraction of decomposed organic matter (leonardite) that is soluble at all pH ranges (high to low) and in water.
Humic acid	The fraction of decomposed organic matter that is only soluble at a high pH and insoluble at a low pH.
Humin	The fraction of decomposed organic matter that is insoluble at any pH, low or high.

This process can be better illustrated by explaining how a batch of humic acids is made from leonardite:

- 1st – Leonardite is mixed with water and the pH is raised to 12.0 (on a scale of 0-14) and the mixture is mixed for a few hours to several days.
- 2nd – The mixture is allowed to stand and settle (or filtered/centrifuged) until the insoluble material settles out. This is the "humin". (Also includes clay, silt, sand and other impurities)
- 3rd – The solution that is left is referred to in the industry as "humic acids" (plural) which is the fulvic and the humic together. If fulvic is desired, the solution is lowered to a pH of 1.5 to 2.0 and all the humic then settles out. The yellow to orange solution that is left is referred to as "fulvic acid"
- 4th – The black material that settled out of the 3rd step can be re-solublized by raising the pH back up to 10-12. This is the "humic acid"

Some commercial producer(s) of humic acids promote that the product includes the "humin" fraction, which if true, would likely have limited direct biological activity. It is possible that what is referred to as "humin" has actually been chemically altered to become more soluble, or has been stabilized in a colloidal suspension.

Humic acids are very complex (large) molecules and in reality there is no definite line between "fulvic" and "humic" as above described. There are properties of humic acids and how they chemically behave in solution, but really they are a steady progression of more and more complex molecules from the simplest "fulvic" molecule to the most complex and large "humic" molecule.

One of the most important methods of characterizing and understanding humic acids is the understanding and study of the "Molecular Weight" (size) of various humic molecules and comparing various sources of humic in regards to molecular size distribution.

Molecular Weights of Humic Substances

What is "molecular weight"?

> The sum of the atomic weights of the atoms that make up the molecule. In simple terms, water has a molecular weight (MW) of 18.
>
> H_2O is (Hydrogen X 2 X At. Wt. of 1 = 2) + (Oxygen X At. Wt. of 16) = 18

As with other classification attempts on humic substances, the area of molecular weight measurement also shows a degree of variance in results depending on the type of extraction, origin of material and degree and method of purification of the samples. One of the most feasible methods designed to determine the molecular weights of humic materials is gel filtration, in which the humic molecules are divided into respective fractions based on size. Similar results can be obtained by utilizing ultrafiltration or ultracentrifugation methods.

Effect of extraction on molecular weight – This type of research has resulted in valuable information regarding the effect of various extractions used in the industry. The standard sodium hydroxide or potassium hydroxide chemicals used by many companies producing humic acid products, results in the highest molecular weight fractions and the most impurities in the final product in comparison to other extraction procedures. There are even a few papers comparing the effect of sodium and potassium hydroxide on soft lignite deposits in which up to 85% of the carbon was extracted. In molecular weight comparisons, potassium hydroxide at the proper concentrations did result in the widest range in molecular sizes. However, prolonged storage at high pH levels did result in a decrease of low molecular weight humic compounds.

Extraction & processing procedures – Regarding extraction procedures, companies that process coal derived humic acids, are often concerned about the percentage of material extracted from the source. Although it is more economically feasible to have a high extraction percentage, it is more important to extract the most bioactive molecules then the greatest volume.

Furthermore, in the scientific analysis of humic materials, scientists are interested in extraction procedures that extract the highest percentage of the humic in the sample without damaging its original structure. In agriculture, we cannot possibly supply soil HUMUS by applying humic materials, (not only in structure, but also in volume), so the focus must be on extracting valuable, reactive "chemicals" that produce beneficial results when applied to soils and crops.

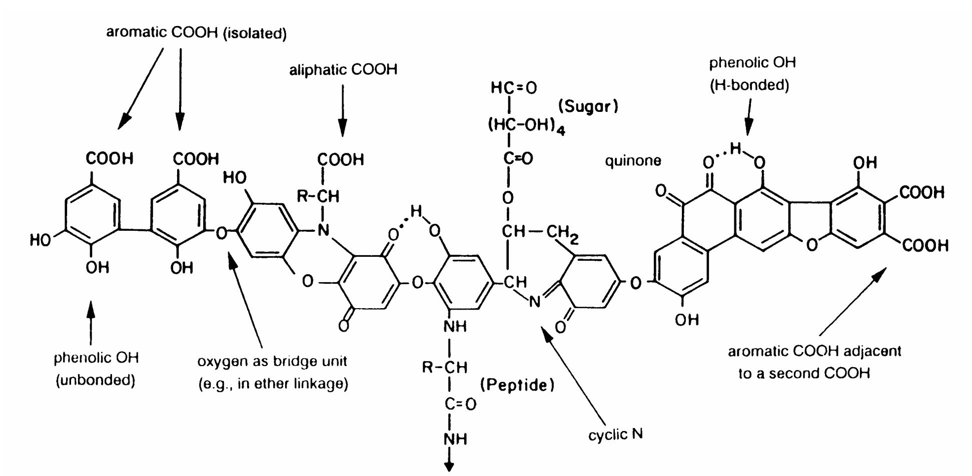
Conclusion: Humic acids should be extracted for the PURPOSE they are to be used for, and NOT the "percentage" in the product. The FORM (size, C : O ratio, etc.) should be the primary objective of extraction and processing procedures.

Biological Activity – Research comparing concentrations and molecular size of humic substances, reveals the activity of the lower molecular weight fraction of humic acids. To some researchers, these low molecular weight fractions are considered the "aromatic" core of the humic molecule. For example, the effect of humic acid on the elongation of pea root segments was consistent at low concentrations and inhibitory at higher concentrations.5 This can indicate that it is not the concentration (percentage) of humic acid content in a product that is important, but the presence of low molecular, biologically active cores.6 Controlled studies of the effect of humic acids on enzyme activity in aseptic conditions (no microbial action), demonstrates that humic acids with a molecular weight of less than 50,000 have the most positive effect in low concentrations.7 In other studies, the humic/fulvic mixtures that had a molecular weight of less than 10,000 had a much greater effect on plant growth than those with a molecular weight of 10,000 to 100,000.8

Fulvic acid is a lower molecular weight than the humic acid fraction. It is estimated that fulvic acid ranges from 300 to 10,000, while humic acids are found in sizes from <5,000 to over a million. Of importance to agriculture, it is estimated that the average molecular weight of humic solutions extracted progressively increases from water to soil to peat to lignite coal.9

A "Picture" of a Humic Acid Molecule

Many debate the actual structure of these molecules, however, one commonly acceptable hypothetical structure is presented as follows:4



However, before one assumes that this is actually a "picture" of a humic acid molecule, let us do some calculations. The approximate molecular weight of the above pictured compound (excluding potential "R") is less than1,800. This would mean that the above picture is more representative of a fulvic acid molecule. Some in the humic acids industry try to peddle this structure as a humic molecule; however, one would have to "paste" a great number of this "pictured" compound together to get a true view of a large humic acid molecule. Especially molecules extracted from lignite or leonardite.

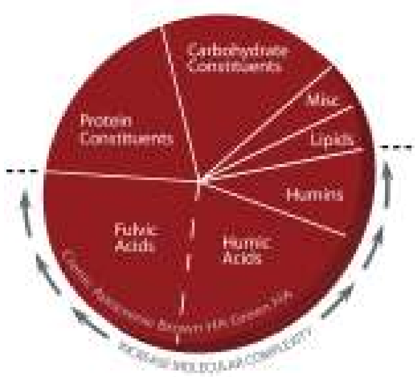
Humic Acids – Soil Humus?

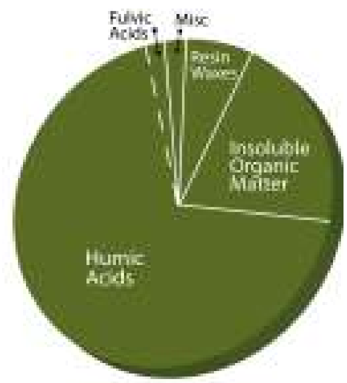
A study of soil humus, the source and foundation of much of the humic acids literature, soon reveals that it is much more complex than a simple extraction of leonardite. Furthermore, soil humic acids are even *different* than leonardite humic acids.

A striking difference is the % carbon and % oxygen:

	Avg. Range in Percent Carbon	Avg. Range in Percent Oxygen
Lignite Humic Acids	60% to 65%	27% to 30%
Soil Humic Acids	53% to 56%	32% to 36%

Even more important the "other" constituents of soil humus, which is represented by the pie chart on the left, compared to standard humic on the right.





In soils, microorganisms also synthesize humic substances. Many studies have been written on the subject. For example, Martin *et al* (1967), produced "humic acid" with *Epicoccum nigrum,* and compared some of their characteristics to leonardite humic acids.10 in a purified form, both humic acids resisted decomposition well, 5% to 13% and 1 % to 7%, respectively in eight weeks. However the *E. nigrum* extract contained components the very susceptible to microbial breakdown, 20% to 50% in eight weeks. The *E. nigrum* humic acids contained 53% to 59% carbon (found in soils), while leonardite contained 59% to 60%. In soil aggregation studies, *E. nigrum* humic acids improved stability by 30%, while the leonardite humic acids resulted in a 16% improvement, both at 0.5% concentration.

At Bio-Gro, Inc., we have used this information to improve the quality and field performance of our products. CHB Amino 21 is a product containing humic/fulvic acids, amino acids (protein), complex carbohydrates (not simple sugars), organic acids and various other microbial co-metabolites. This product has not been fashioned after any particular soil type or humus fraction, but field responses due show an advantage of adding these compounds.

What are Humic Acids supposed to do?

All factors being constant (temperature, moisture and nutrients) soil, rich in humus, will out produce in yield and quality soil low in humus content. These humic substances play some very important roles in the production of crops:3

1) Physical condition of soils, aggregation of soil particles
2) Affect the availability of nitrogen, phosphorus, sulfur & minerals
3) Have an "auxin" like growth effect on plants & roots
4) Act as a source of energy to soil microorganisms
5) Important in nutrient exchange capacity of soils
6) Interact with organic chemicals and toxic pollutants

Do not be trapped into thinking that all humic materials are alike. The above description applies to humic substances found in soils, as does much of the published research on the subject. Therefore, it should be stated, that a simple alkaline extraction of leonardite or lignite, as sold commercially, will not necessarily cause an improvement in soil fertility and show all the positive effects as described above.

There are a lot of claims made about commercial humic acids that are not necessarily accurate, but nevertheless decades of application experience has demonstrated that commercial humic acid products to have agricultural value.

At Bio-Gro, Inc., our research and field demonstrations programs have shown that liquid humic acids (especially our product) have viable uses, especially in nutrient uptake;

- Humic acids are known to help phosphate uptake, many humic/phosphate blends show viable responses, especially in calcareous soils.

- Humic acids are known to increase trace mineral availability, again especially in high pH soils, likely due to complexion of micronutrients.

- Humic acids help plants growth in high soluble sodium soil environments.

- Humic acids, especially those found in Bio-Gro products, have demonstrated the ability to increase sap-calcium thereby triggering rooting responses.

- Humic acids can help uptake of most nutrients, including potassium, especially when applied during and prior to bloom.

- Humic acids should be applied at rates of 5-15 gallons per acre; most growers do not use enough.

The Effect of Added Humic Substances on Plants & Soils

It is estimated that prairie soils lose up to 50% of their organic matter in the first 3-5 years of cultivation.[12] Although returned crop residues are beneficial, they do not form stable humus compounds under continued cultivation.

Do you need to add humic acids? The answer should always be based on proven field economics, but in most cases the addition of humic acids with commercial fertilizers is beneficial.

There are numerous scientific publications showing that extracted humic acids show plant growth responses.

A good published summarization[11] shows that different sources do cause different responses, that the most effected nutrients are P and Fe and that the best responses are in low organic matter soils.

Plant growth responses are often attributed to the ability of humic acids to complex micronutrients due to chelation ability, which increases with pH.[13]

At pH 5, little complexing occurs, while at pH 8, 50 mg/l humic acid will complex 2.1 mg/l of iron.[14] The increase is likely due to the increased dissociation of humic acids molecules at high pH values.

"Young" humic acids (compost) can contain certain polyphenols that are capable of reducing ferric iron to the ferrous state.[15]

At little known effect is that low molecular weight compounds enter the plant during early stages of growth and are supplementary sources of polyphenols that serve as respiratory catalysts.[16]

Humic substances, specifically fulvic, is known to protect auxin levels by limiting IAA-oxidase activity.[17]

Direct stimulation of rooting and adventitious root formation has been long attributed to fulvic acids, especially those extracted from soils.[18]

Low molecular weight humic compounds, especially water soluble fractions, are shown to stimulate nitrate uptake via stimulation of root plasma membrane ATPase activity.[19]

Generally speaking, volumes of literature point out that humic substances have numerous plant growth and soil quality characteristics. The question is, how do these compare to the humic substances for in commercial humates? The most important answer lies in the solubility of the humic compounds and the molecular size.

Conclusion

The first and foremost point is that humic acids (from leonardite) are only a part of a complete nutrition system. If you are a product formulator and/or a soil fertility expert wishing to give your grower the best possible return on his crop inputs, you must consider a complete nutrition approach!

This approach should contain humic acids as part of the program. Following are some important characteristics that you should consider;

1) Humic acids can only be purchased in small quantities, compared to what is really needed for soil fertility. Consider that a 3% organic matter soil is 60,000 lbs/acre foot of organic matter. If 10% (6,000 lbs) of this organic matter is humic acid, how much humic acid can you afford to put on? Therefore, humic acids should always be mixed with fertilizers!
2) Humic acids work best on low organic matter (less than 2%-3%) soils.
3) Make sure your humic acid is soluble in fertilizer. To test this, put a small amount in the fertilizer solution and shake up. Let it stand for a few days and see how much settles out and how. When mixed NO particles should be noticed. If any particles are visible to the eye, what type of coverage are you really getting?
4) There should be some information available on the molecular size range of the humic acid you are using.
5) Consider addition of other soil organic matter components to fertilizer solution; mainly protein (amino acids) and complex carbohydrates.
6) Lastly, remember the golden rule: Humic acids help plants take up nutrients; they need a balanced and COMPLETE fertilizer program to work effectively.

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