

## A REVIEW OF HUMUS AND HUMIC ACIDS

by

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### INTRODUCTION

The term "humus" dates back to the time of the Romans, when it was frequently used to designate the soil as a whole. It was later applied to the organic matter of soils and composts or to different fractions of this organic matter, as well as to complexes formed by the action of chemical reagents upon a variety of organic substances.

Wallerius first defined "humus" in 1761 in terms of decomposed organic matter. However, the prevailing ideas concerning the chemical nature of humus and the mechanism of its formation were very vague. Most often it was considered as a complex formed in soils, in bogs, or in composts, from plant residues, by a special process of "humification."

De Saussure, in his famous work, "Recherches Chimiques Sur La Vegetation", devoted considerable attention to humus. He found that it is not a homogeneous substance, but that it consists of various complexes which can be readily removed. Thaer differentiated between "acid humus" or peat, formed with limited admission of oxygen, and "mild humus", formed in the presence of sufficient oxygen. Liebig spoke of "humus" as "a brown substance, easily soluble in alkalis, but only slightly soluble in water, and produced during the decomposition of vegetable matters by the action of acids or alkalis."

The term "humus" came into general use at a time when organic chemistry was still in its infancy and when all organic and inorganic compounds were considered to be substances very simple in chemical composition

Waksman defines humus as "a complex aggregate of brown to dark colored amorphous substances, which have originated during the decomposition of plant and animal residues by microorganisms, under aerobic and anaerobic conditions, usually in soils, composts, peat bogs, and water basins". Chemically, humus consists of certain constituents of the original plant material resistant to further decomposition; of substances undergoing decomposition; of complexes resulting from decomposition, either by processes of hydrolysis or by oxidation and reduction; and of various compounds synthesized by microorganisms. Humus is a natural body; it is a composite entity, just as are plant, animal, and microbial substances: it is even much more complex chemically, since all of these materials contribute to its formation.

Coal represents a number of humus types in an advanced state of decomposition, produced from various plant residues at different periods during prehistoric times, and later stratified and compressed by superimposed layers of mineral matter.

The mechanism of coal formation, through the peat state, is commonly explained as follows: Peat changes first to lignite, the latter to bituminous coal and finally to anthracite, through the action

of heat, as a result of which, fractional distillation takes place. The brown coal or lignite's differ considerably in mode of occurrence and in their physical and chemical properties, thus the variation in amount of humic acids found in different deposits. Studies of the chemical processes involved in the formation of coal led to the various hypotheses concerning the "humic acids", "ulmic acids", "humins", "ulmins", and "fulvic acids". It is generally accepted that microorganisms have played a prominent part in the process of coal formation.

### The Importance of Organic Matter

Soil formation is closely linked with the action of diverse forms of organic substances on the parent rock. The pioneers in this process (biogeochemical) are apparently microorganisms, whose participation in the natural circulation of iron, sulphur, calcium, silica, phosphorus, and other elements has been shown by many investigators.

In the production of a fertile soil, organic substances play a direct part as they are the sources of plant nutrients which are liberated in available forms during mineralization. But organic substances also play an indirect role.

Besides being a source of nutrients for the plant, and the most important factor in structure formation, organic matter has also a fundamental effect on the physical properties of the soil (water-holding capacity) and determines to a large degree such physico-chemical properties as the exchange capacity and buffering properties; these properties are of great importance, not only in controlling the uptake of nutrients by the plant and their retention in the soil, but also in suppressing the deleterious effect of soil acidity. There is also conclusive evidence that quite small amounts of certain organic substances (highly dispersed humic acids) have a definite, positive effect on the growth and development of the plant. Much research is still needed to understand the mechanism of the process.

### The Role of Humic Acids

The value of regular additions of organic matter to the soil has been recognized by growers since prehistoric times. However, the chemistry and function of the organic matter has been a subject of controversy since men began their postulating about it in the 18th century. Until the time of Liebig, it was supposed that humus was used directly by plants, but, after Liebig had shown that plant growth depended upon inorganic compounds, many soil scientists held the view that organic matter was useful for fertility only as it was broken down with the release of its constituent nutrient elements into inorganic forms.

At the present time most soil scientists hold a more moderate view and at least recognize that humus influences soil fertility through its effect on the water-holding capacity of the soil. Also, since plants have been shown to absorb and translocate the complex organic molecules of systemic insecticides, they can no longer discredit the idea that plants may be able to absorb the soluble forms of humus.

Over the last 150 years much has been learned about the chemistry of organic matter. Some of the earliest work by Sprengel on the fractionation of organic matter still forms the basis of methods currently in use. These methods utilize dilute sodium hydroxide (2 percent) to separate humus as a colloidal sol from alkali-insoluble plant residues.

From this humus sol, the humic fraction is precipitated by acid which leaves a straw-yellow supernatant, the fulvic fraction. The alcohol soluble portion of the humic fraction is generally named ulmic acid.

More recently, chromatographic, spectrophotometric, and X-ray analyses have added much to our knowledge about the organic structural groups present in humus. The reactions of the cation and anion exchange sites have also been extensively studied. However, there has been little attempt to establish a relationship between the chemistry and the soil fertility attributes: buffering, chelation of essential elements, and hormone effect of organic matter from the same source.

Kononova, writing in the U.S.S.R., where humus appears to be a favorite research topic, makes some very extravagant claims for the effects of humic acids in the soil. She has reported at length on the beneficial effects of humus on soil fertility and plant growth, but has largely ignored the data of those workers who failed to get a response to humus, or else got a detrimental effect. However, a brief glance at the literature reveals some contradictory results; and for every reference to the success of humus could be given a reference to its failure. It is obvious that out of that broad group of soil substances which may be separated by alkaline extraction, the humic acids; there are some which promote soil fertility and some which do not.

Jenkinson and Tinsley have shown that ligno-proteins (humic material) from different sources have very different infrared spectra; and Makstnow and Liwski have demonstrated differences in plant response to humic fertilizers according to their method of preparation. It is therefore to be expected that the source and method of extraction would be especially important in deciding the soil fertility potential of the humic acids.

Recent work on the chemistry of leonardite, an oxidized form of lignitic coal, revealed it to be mainly composed of the mixed salts of humic acids. The availability of commercial quantities of humic acids for the first time makes a series of studies on both the chemistry and the soil fertility attributes worthwhile.

Humic acids are colloids and behave somewhat like clays, even though the nomenclature suggests that they are acids and form true salts. When the cation exchange sites on the humic molecule are filled predominantly with hydrogen ions, the material is considered to be an acid and is named accordingly. However, it has no great effect on pH because the acid is insoluble in water. When the predominant cation on the exchange sites is other than hydrogen, the material is called humate. The humates of monovalent alkali metals are soluble in water, but the humates of multivalent metals are insoluble. Apart from their effect on the solubility of the materials and their absorption by clays, the different cations have little effect on the humic molecules.

### **The Action of Humic Substances**

Strictly humic substances participate actively in the decomposition of rocks and minerals. The decomposition of various minerals by solutions of humic acids has been demonstrated by many investigators. The character of the action depends on the nature of the humic substances, as well as on the resistance of the minerals.

Humic substances, like organic compounds of an individual nature, promote the conversion of a number of elements into forms available to plants. The increased availability of P<sub>205</sub>, in the presence of humic acids has been well documented. The

effect of humic acids on the conversion of iron into available forms protecting plants from Chlorosis even in the presence of a high P<sub>205</sub> content, was demonstrated by DeKock in 1955. In the supply of trace elements and rare elements to plants, an important role is played by compounds in which they are linked with humic substances in the form of chelates.

Numerous reports are available on the presence of auxin type reactions by humic substances. It is also well established that humic substances increase the germination capacity of seed and the vitamin content of plants.

Lieske reports that humic acids and their derivatives increase the permeability of plant membranes, so promoting the uptake of nutrients.

Many investigators have observed a positive effect of humic substances on the growth of various groups of microorganisms. They attributed this effect to the presence of iron in the humic acids or to their colloidal nature, or they regarded humic substances as organic catalysts.

In experiments on the infiltration of NH<sub>4</sub>NO<sub>3</sub> into sunflower leaves, the presence of humic acids was found to increase the percentage content and total amount of nitrogen. Humic acids in small amounts act as specific sensitizing agents, increasing the permeability of the plasma and resulting in an increased uptake of nutrients by the plants; in large amounts humic acids are a source of available iron.

Khristeva believes that humic acids entering the plant at early stages of development are a supplementary source of polyphenols, which function as respiratory catalysts. This results in an increase in the living activity of the plant: enzyme systems are intensified, cell division is accelerated, root systems show greater development and, ultimately, the yield of dry matter increases.

The manifold effect of humic substances on the plant, shown both in the external medium and in the biochemical processes occurring in the plant, has been well demonstrated.

In the methods of preparation and application of humic fertilizers, much research is still needed. The general principles arising from theoretical arguments are: the presence in the fertilizers of substances of quinoid nature exerting a stimulating effect on plants; the possibility that humic substances are converted into a highly dispersed state, favoring their penetration into the plant. The small amount of humic fertilizer cannot be regarded as a main fertilizer: their stimulating effect is only observed in the presence of an adequate supply of the major nutrients--nitrogen, phosphorus, and potassium.

There is a growing interest in the use of organic materials as fertilizers or soil amendments. This may be attributed to: 1) an interest in the reduction of the use of chemical fertilizers; 2) public concern for the potential polluting effects of chemicals in the environment; and 3) a pressing need for energy conservation. The research reported herein was conducted in an effort to explore humate material as one of the organic natural resources with the potential for meeting some of these needs.

**Reference:** Senn, T. L. and Alta R. Kingman, 1973, A review of Humus and Humic Acids. Research Series No. 145, S. C. Agricultural Experiment Station, Clemson, South Carolina.