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# Humic Substances and their Role in the Environment

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## Biography

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## Abstract

The article provides a general information regarding humic substances, their structure, formation and role in the environment. Humic substances increase the quality and productivity of soil by improving soil structure, water retention and ensuring constant access to the nutrients. They also block and deactivate elements and chemicals occurring in harmful concentrations. In aquatic systems they remove toxic elements, organic chemicals of anthropogenic origin and other pollutants as well as directly and indirectly affect water organisms. Additionally, humic substances and artificially produced humic products indicate plant and animal bio-stimulatory effects, due to what they are used in agriculture, pharmaceuticals and medicine.

***Keywords:*** *Humic Substances; Productivity of Soil; Soil Structure, Water Retention*

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## Introduction

Humic substances, commonly referred to as humus, are considered to play a crucial role in the terrestrial and aquatic systems [1], affecting also human health, what was already known in antiquity. All the great ancient cultures were depended on agriculture for which soil quality and prevention of its exhaustion were absolutely critical. Despite the fact that no composting processes of organic components were known that times, organic remnants were commonly introduced into the soil to improve its fertility. Humus as an organic fecundity substrate of the Earth excited thinkers from the ancient times and stimulated both solid research and charlatanry, not only connected with agriculture. First descriptions of medical applications of humus can be found in Sanskrit and also ancient writings of Rome and China. On the other hand, in ancient Egypt straw was mixed with mud to produce stronger bricks that are less likely to break or lose their shape. This procedure was used even though the ancients builders did not realize that an improvement of bricks properties was connected with humic substances released from the straw that created organo-mineral complexes increasing plasticity of the clay.

Despite nearly mystic reverence and enormous interest, the history of research on humic substances has only somewhat more than two hundred years. For the first time they were extracted from peat by the Franz Achard in 1786, who was German chemist known from the discovery of sugar production from sugar beets. In the mid-nineteenth century, the Swedish chemist Jacob Barzelius also studied the chemical properties of organic substances isolated from spring water. The significance of humic substances in soil productivity was emphasized in the end of the $19^{th}$ century by the great soil scientist, VV Dokuchaev. His research on Chernozems, distributed in southern Russia, pointed out that humic substances content positively influences soil productivity and plant growth. Since then, humic substances research from the agronomical point of view continues to be one of the major topics in modern soil science.

In addition, humic substances can also function as carriers of pollutants, thus controlling the fate of both organic and inorganic xenobiotics. Regardless, studies on carbon dynamics related to climatic change have shed light over the quality of humic substances affecting persistent carbon reserves in terrestrial environments. For this reason, knowledge on the physical and chemical properties of humic substances are considered to be valuable from a variety of environmental aspects. Over the past few decades, the fate of humic substances attracted an increased interest of researchers in many different fields of science, including soil scientists, water scientists, chemists, environmentalists, plant physiologists, pharmacists and others. In 1981 the International Humic Substances Society (IHSS) was founded to bring together scientists in the coal, soil, and water sciences with interests in humic substances. The Society is recognized as a world leader in fostering scientific education and research and promoting public understanding of humic substances (http://humic-substances.org). The motto of the IHSS is "To advance the knowledge and research of natural organic matter in soil and water". Undoubtedly, a driving force for the growing interest in humic substances, is the increasing awareness in their immense role in terrestrial and aquatic systems, as well as their bio-stimulatory effects on plant growth. In "Chemical Abstracts" - the world's largest chemical scientific database, more than 2,000 articles are published annually devoted to the possibilities of these unusual substances.

### Nature and forming of humic substances

Humic substances are complex organic substances of soil formed in the process of humification, which is responsible for fossil coal, oil deposits and others. It is the second, after photosynthesis, greatest organic process on the Earth. It is estimated that as a result of photosynthesis, more than 5,000 tons of atmospheric carbon are bound each year, while the transformation of dead living organisms results in the production of about 4,000 tons of carbon, collected annually on the surface of the Earth. Humic substances represent a class of naturally occurring organic substances being created as a result of biochemical, chemical and physical transformation of dead plant, microbial remains and fauna debris. Formation of humic substances is connected with activity of microorganisms, which utilize and break down organic substances and lead to accumulation of recalcitrant macromolecular compounds of specific properties. When microorganisms die, they are themselves broken down and added to the recalcitrant humic mass. These progressive decay and biotic and abiotic transformation processes form a complex and heterogeneous mixtures of polydisperse materials, being a mayor constituent of the natural soil organic matter. The genesis of humic substances can take hundreds or even thousands of years and leads to their high variety. Because humic substances are produced from various sources of organic matter, they are highly heterogeneous in composition, structure, polydispersity and sizes. This distinguish them from naturally occurring bio-molecules such as proteins, carbohydrates, lipids and other.

The research of humic substances is complex because these organic compounds are bound by (or associated with) soil mineral fractions and require physical and/or chemical separation from the inorganic components through an extraction procedure, prior to their physico-chemical analysis. According to classic approach [2], humic substances are classified into three fractions based on water solubility: (1) fulvic acid is soluble at all pH conditions; (2) humic acid is insoluble under acidic conditions but becomes soluble at higher pH; (3) humin is the fraction not soluble in water at any pH value. This classification is commonly accepted and adopted by soil organic matter researchers [3,4]. Through this viewpoint humic acids were defined as organic substances extracted from soil that coagulate when a strong-base extract is acidified, whereas fulvic acids are organic acids that remain soluble at the mentioned conditions. Despite long study, molecular structure and chemistry of humic substances remains elusive. The traditional view is that humic substances are heteropolycondensates, in varying associations with clay minerals. A more recent view is that relatively small molecules also play a role [5], as these heterogeneous molecular components of the soil organic matter are auto-assembled in supramolecular associations and synthesized by biotic and abiotic reactions in soil. Humic substances are highly chemically reactive yet recalcitrant with respect to biodegradation. Most of the data on humic acids, fulvic acids and humin refer to average properties and structure of a large assembly of components of diverse structure and molecular weight.

Among the various organic substances occurring naturally, humic substances are the most widespread. They represent about 25% of the total organic carbon on the Earth and can be found in various environments such as soils, rivers, lakes, sea sediments, peats and coals, especially low-grade coal. The last one, called leonardite, is a source of humic substances extracted in a commercial scale to obtain humic products used in agriculture and for other purposes. In terrestrial and aquatic systems humic substances affect the chemistry, cycling and bioavailability of chemical elements, as well as transport and degradation of xenobiotic and organic chemicals of natural origin.

## Role in terrestrial environments

Humic substances are considered to play a crucial role in the terrestrial ecosystem. Soils contain more organic carbon than the atmosphere and vegetation combined together; therefore, mineralization of soil organic matter and release of carbon versus humification processes, could greatly affect carbon capture and stabilization, and consequently the global climate change. Humic substances are known to be the most important component of soil, and they are crucial to human welfare due to their role in generating food, animal's feed and fiber. They closely relate to the biogeochemical cycling of nutrients, anthropogenic organics as well as some polluting elements. Humic substances are able to affect contaminant uptakes by crops and/or leaching into groundwater. Studying the interactions of heavy metals or organic compounds with humic substances provides insights into pollutant mobility, behavior and fate, and allows better understanding of natural mitigation phenomena and potential impact on the environment.

Humic substances are accumulated in the surface horizon of soil, contributing to its black color. In the leaf litter or composts, their color may be yellowish-brown to black, depending on the degree of decay and concentration. Due to the role of humic substances in many complex chemical and biochemical reactions in soils, they largely determine soil quality, and they are vital to maintaining soil fertility. The ability of fulvic and humic acids to dissociate $H^+$ ions from various functional groups (mostly carboxyl and phenolic) results in a wide array of different negative charges. This markedly contribute to the soil cation exchange capacity, ensuring plants access to nutrients, which is controlled in 50 to 90% by humic substances. The sorption capacity of humic substances, especially fulvic acids, exceeds by far (up to a factor of ten times) the sorption capacity of soil mineral components and often dominates their sorption properties, especially in sandy to sandy loam soils. Due to that they play a crucial role in the inactivation of pesticides, heavy metals and other polluting agents. Humic substances also have a decisive impact on the pH buffering capacity of soils. Binding of metals to carboxyl and phenol sites in humic substances enabled numerous modeling of metal retention and mobility in soils. Studies on the role of humic substances in Fe supply to plants provide another illustration of the importance of these substances in metal ion retention and transport. Calcareous soils are known for iron deficiency for plants, however supply of this element in a complexed form with humic substances can distinctively and positively affect plant growth and increase chlorophyll concentration in the leaves [6].

Furthermore, humic substances affect physical, chemical and biological properties of soils to a much greater extent than the other soil mass constituents. An increase in their content, especially that of humic acids in the presence of Ca, causes the formation of stable aggregates, which in turn, positively affects field water capacity, air capacity, porosity and permeability of different soil types. Thus, extensive loss of humic substances, especially humic acids, contribute to an increase of soil compactness, a decrease of soil aeration and a consequent occurrence of reductive chemical conditions. Among others, the dark color of humic substances causes enhancement of sunlight absorption, and improvement of the thermal properties of soils, what is crucial especially at the beginning of the growing season. Humic substances also induce root proliferation and modify the architecture of the root system. As a result, they stimulate plant growth and development. Due to that, currently, humic substances are commonly used as organic amendments for agricultural soils.

### Role in aquatic environments

Aquatic humic substances contain only humic acids and fulvic acids. Sea waters contain 0.1 to 3 mg of organic matter per liter, while their content in fresh waters reaches up to 20 mg per liter. These components are generally removed from water by lowering the pH to 2 and adsorbing both components on a suitable resin column. Then humic substances are extracted from the resin with strong base followed by lowering the pH to 1 to precipitate the humic acids. The resin column separation is also used to separate fulvic acids from the non-humic materials (amino acids, peptides, sugars, etc.) extracted from soils. At low pH the fulvic acids adsorbs on the resin, but non-humic materials pass through the column.

In aqueous systems, like rivers, streams and likes, about 50% of the dissolved organic materials are humic acids, which affect their pH. Humic substances are a major source of organic carbon in aquatic systems, thus they are extensively investigated by the community of chemists. Aquatic carbon is not only important as a part of the global carbon cycle, but also for local biogeochemical processes in water bodies. Water humic substances directly and indirectly, affect aquatic ecosystems, as well as living organisms. On the long-term basis, dissolved humic substances affect primarily the physical and chemical properties of waters and can act as the most important natural neutralizing components in these environments, e.g. by stimulating biotransformation of xenobiotics. On the short term basis, they can act as a source of organic nutrients and also exhibit the capacity to regulate the bio-concentration and toxicity of xenobiotics and heavy metals. Dissolved humic substances are a major factor affecting the optical properties of natural waters. They have a direct impact on both the quantity and quality of light in waters, affecting water biota life and development. The strong specific UV absorption renders humic acids like a natural biogeochemical filter against specific UV radiation.

An important issue is the chemical removal of pollutants by humic acids in water treatment and water purification technologies. On the other hand, humic acids are considered to act also as contaminants due to their reactions with disinfectants which can generate by-products that are toxic to humans. Humic substances dissolved in ground waters can influence the release of toxic elements from sediments. For example, the exposure of more than 50 million people in communities in South Asia to toxic levels of dissolved arsenic in groundwater supplies is considered to be the greatest mass poisoning in human history [7]. This exposure was the inadvertent consequence of the introduction of shallow tube wells to access groundwater supplies in extensive wetland regions underlain by sediment from the Himalayas, from which arsenic was released due weathering. In the sediments, the As is associated with iron oxides and is released into the groundwater through reductive dissolution of the oxide surfaces driven by microbial respiration of labile organic substrates. Humic acids dissolved in these groundwaters can influence the release of arsenic from sediments by both forming complexes with As and by acting as an electron shuttle.

### Plant and animal bio-stimulatory effects

Organic soil amendments have been known by farmers to be beneficial to plant growth for longer than the history recorded that. However, the chemistry and function of the organic matter have been unclear for centuries. Until the time of Justus von Liebig, nineteenth-century chemist called the father of fertilizers, it was believed that humus was used directly by plants. After Liebig showed that plant growth depends upon inorganic compounds, many soil scientists shared 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, soil scientists hold a more holistic view and at last recognize that humus influences soil fertility through its effect on several soil properties. 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.

In the recent decades, there has been a growing interest in artificial humic products obtained mainly by alkaline extraction of leonardite (the oxidized version of lignite obtained in open mining). Industrial humic preparations produced from natural resources largely inherit the properties of humic substances from the original raw materials and act as the soil ameliorants or plant growth regulators [8]. Studies on the use of humic products addressed mainly their effects on plant yield and quality as well as the physiological properties of plants [9]. Many research has shown that the use of humic products stimulate growth of roots, leaf and shoot, increase the uptake of nutrients [10] and improve plant resistance to stress [11]. It is believed that humic substances can regulate the absorption of soluble nutrients, affect plant metabolism, mainly by stimulating and regulating enzymes, and thus may also act as inhibitors or enzyme activators [12]. In turn, other studies show that humus-enzyme interaction may lead to a decrease in enzyme activity [13]. They may also modulate transport through plasma membranes, resulting in increased efficiency of some intracellular processes [14]. It is also known that humic substances may act as a limiting factor on the development of certain pathogens [15].

Currently, increasing research efforts are directed at determining crop management practices that can improve soil health in economically viable manners. Soil health is widely thought to benefit from increased organic carbon availability in soils. When soil humus percentages falls below 2%, the soil cannot provide sufficient quantities of humic materials into the crops grown for the amounts needed by the living organisms.

Finally, humic substances preparations, named humate, are commonly used as an animal nutritional supplement. They contain both humic and fulvic acids. The fulvic acid is the chelator that carries the minerals. The humic acid acts as dilator increasing the cell wall permeability. This increased permeability allows easier transfer of minerals from the blood to the bone and cells [16]. What's more, humic substances can be used successfully also in medicine [17]. They can act as antiviral and anti-inflammatory agents; have uses in wound healing, cancer and prion disease therapy; and exhibit antimutagenic/desmutagenic potential. They can be used as antiviral and anti-inflammatory agents, they also have antimutagenic potential, and are also used in wound healing, prion diseases and cancer treatment.

## Conclusion

Among the various organic substances occurring naturally, humic substances are the most widespread, present in soil, water, geological organic deposits such as lake sediments, peat, and coal. They represent about 25% of the total organic carbon on the Earth and comprise up to 50 - 75% of the dissolved organic carbon in water. Humic substances are of unquestioned importance to multiple environmental processes in both soil and aquatic systems. Humic substances increase the quality and productivity of soil by improving soil structure, water retention and ensuring constant access to nutrients. They also block and deactivate elements occurring in toxic dose. In aquatic systems they remove toxic elements, organic chemicals of anthropogenic origin and other pollutants as well as directly and indirectly affect water organisms. Finally, humic substances are successfully used in medicine and pharmaceuticals.

## Bibliography

1. Tan KH. "Humic matter in soil and the environment: principles and controversies". 2nd edition. Boca Ranton: CRC Press (2014).
2. Stevenson FJ. "Humus chemistry. Gensis, Composition and Reactions". John Wiley & Sons.New York (1982).
3. Swift RS. "Organic matter characterization". In: Sparks DL., *et al*. (Ed.), Methods of Soil Analysis. Part 3. Chemical Methods. *Soil Science Society of America* Inc., Madison, WI (1996): 1011-1069.
4. Weber J., *et al*. "Preface: Humic substances in the environment". *Journal of Soils and Sediments* 18 (2018): 2665-2667.
5. Piccolo A. "The Supramolecular structure of humic substances. A novel understanding of humus chemistry and implications in soil science". *Advances in Agronomy* 75 (2002): 57-134.
6. Chen Y., *et al*. "Mechanisms of plant growth stimulation by humic substances: the role of organo-iron complexes". *Journal of Soil Science and Plant Nutrition* 50 (2004): 1089-1095.
7. Olk DC., *et al*. "Using Humic Fractions to Understand Natural Organic Matter Processes in Soil and Water: Selected Studies and Applications". *Journal of Environmental Quality* 48 (2019): 1633-1643.
8. Yakimenko OS and Terekhova VA. "Humic preparations and the assessment of their biological activity for certification purposes". *Eurasian Soil Science* 44.11 (2011): 1222-1230.
9. Olk DC., *et al*. "Humic products in agriculture: potential benefits and research challenges-a review". *Journal of Soils and Sediments* 18 (2018): 2881-2981.
10. Halpern M., *et al*. "The Use of Biostimulants for Enhancing Nutrient Uptake". *Advances in Agronomy* 130 (2015): 141-174.
11. Berbara RLL and Garcia AC. "Humic substances and plant defense metabolism". In: Ahmad P and Wani MR (Eds.) Physiological Mechanisms and Adaptation Strategies in Plants under Changing Environment. 1. Springer Science+Business Media, New York (2014): 297-319.
12. Trevisan S., *et al*. "Humic substances biological activity at the plant-soil interface from environmental aspects to molecular factors". *Plant Signaling & Behavior* 5-6 (2010): 635-643.
13. Nardi S., *et al*. "Plant biostimulants: physiological responses induced by protein hydrolyzed-based products and humic substances in plant metabolism". *Scientia Agricola* 73.1 (2016): 18-23.
14. Muscolo A., *et al*. "The auxin-like activity of humic substances is related to membrane interactions in carrot cell cultures". *Journal of Chemical Ecology* 33 (2007): 115-129.
15. Yigit F and Dikilitas M. "Effect of Humic Acid Applications on the Root-Rot Diseases Caused by Fusarium spp. on Tomato Plants". *Plant Pathology Journal* 7 (2008): 179-182.
16. Kreutz T and Schlikekewey W. "Effects of implanted bovine calcium hydroxyapatite with humate". *Archives of Orthopaedic and Trauma Surgery* 111.5 (1992): 259-264.
17. de Melo BAG., *et al*. "Humic acids: Structural properties and multiple functionalities for novel technological developments". *Materials Science and Engineering* 62 (2016): 967-974.