Application of Humic Substances in Agriculture

A Partial Bibliography of Recent Humic Literature
Compiled by the Humic Products Trade Association
2011

- Early evidence that humic substances support plant growth

  - Hoagland and Arnon (1950) demonstrated the effectiveness of humic substances when added to Hoagland solution or agar.
  - Early researchers did not know why humic acids had a stimulatory effect on plant growth. Some thought that humic substances extracted from lignite coals contained hormones because of the low doses needed to produce a positive response (Dekock and Sthmecki, 1954).
  - Most of the early research conducted in Eastern Europe on improving nitrogen utilization has not been translated into English (Clapp et al, 2001); however Nardi et al (1996) reviewed and summarized numerous European investigations performed in the late 1900's demonstrating positive impacts on germination and yield of numerous crops.
  - For an extensive review of how humic products are used in agriculture, see MacCarthy and Rice, 1994

- Recent Field Trials

  - A randomized complete block replicated green house and field experiment on grassland pasture, potatoes, and maize showed that the application of liquid and dry humic substances had an overall positive effect on crop yield (Verlinden et al, 2009). The formal meta-analysis revealed an increase in nitrogen, phosphorus, potassium and magnesium in all of the crops, demonstrating a more efficient use of fertilizers. There was a substantial increase in grass production for the treated plants when subject to heat and water stress (drought).
  - Application rate of 60 mg of humic acid per kilogram of soil generated the largest increase in height, weight and nutrient uptake in wheat grown on the soils when compared to applications of 30 and 90 mg/kg. The humic acid application significantly improved soil potassium, phosphorus and nitrate concentrations in both calcareous and non-calcareous soils (Tahir et al, 2011).
  - Brownell et al (1987) reported average yield increases of 10.5% and 11.2% in replicated field trials for tomatoes and cotton respectively, and an average 25% increase in grape production on unreplicated large scale field trials of differing grape varieties in different vineyards.
  - Fernandez-Escobar (1996) studied the effect of a potassium hydroxide extract of Leonardite containing 9% humic acids and 7% fulvic acids on olive trees. Although there was clearly an increase in vegetative growth and enhanced uptake of minerals, there was no statistically relevant effect on yield.
  - A field study demonstrated how the combination of dry calcium with oxidized lignite (Leonardite) combination applied to alfalfa performed as well as the combination of calcium chloride and EDTA, a popular synthetic chelating agent (Pare', et al, 2001).
  - After a thorough review of the literature and performing numerous experiments, Chen et al (2004a) concluded that humic substances at an application rate of 67.5 kg ha^{-1} (59.4 lb a^{-1}) and foliar application of humic and fulvic acids at 375 g ha^{-1} will affect plant growth.

- The addition of humic acids with phosphate fertilizer was studied in a greenhouse trial and then confirmed by field trials on an alkaline soil. Water soluble phosphate was significantly increased in the alkaline soil, increasing the uptake of phosphorus and increasing yield by 25% (Wang et al, 1995).

Modes of Action and Mechanisms

- Enhanced Nutrient uptake

    - The benefits of humic substances in agricultural soils is well established (MacCarthy, 2003), especially in soils with low organic matter (Chen and Aviad, 1990)
    - 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 stimulate microbial activity (see Microbial Stimulants below). Microbial activity directly influences the rate of dissolution from soil rock minerals that are otherwise insoluble (Barker et al, 1997; Welch et al, 2002).
    - Membrane-like bi-layers formed by humic substances surround otherwise insoluble minerals, releasing plant nutrients (Tombacz and Rice, 1999).
    - The bioavailability of nutrients released from soil rock minerals by biological activity is enhanced in the presence of humic substances. (Chen and Aviad, 1990)
    - Humic substances act as a storehouse of N, P, S, and Zn (Frank and Roeth, 1996)
    - Humic substances are known to complex both cations and anions (Huang and Violante, 1986; Mortland, 1986), creating a synergistic effect (Clapp et al, 2001)
    - Humic substances increased nutrient efficiency in maize (Eyheraguibel et al, 2004)
    - Humic substances increased the number of flowers and height of tomato plants (Kaemmerer and Eyheraguibel, 2004)
    - Potassium management using humic substances is more effective when K^+ soil concentration is low (Pinton et al, 1997), which is typical in soils, suggesting that humic substance stimulation of K^+ influx into plant roots is more effective in low-input agricultural systems that utilize low soil concentrations of dissolved nutrients.

- Nitrogen Management

    - Humic acids may improve urea nitrogen use efficiency as well as reducing environmental pollution by increasing soil exchangeable NH_4^+ and available NO_3^- while retaining more nitrogen in the soil (Yusuff et al 2009).
    - In their natural state, humic substances contain anywhere from 1% to 5% nitrogen (Stevenson, 1994). 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)
    - Humic substances have the potential to reduce nitrogen application because of their ability to stimulate soil nitrifying bacteria (Vallini et al, 1997).
    - The importance of humic substances on the fertility of soils and the stabilization of nitrogen has been well documented (Thorn, 2000; Kelly and Stevenson, 1994; Nardi, et al, 1996).
    - 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.
  - Because of their ability to stabilize nitrogen, 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, has recommended the use of humic substances to prevent nitrogen leaching on golf courses (Clapp, 2001).
  - Humic acids stimulate nitrifying bacteria (Vallini et al, 1997)
  - One lab study done by the USDA-ARS at West Texas A&M University suggests that humic substances can be used to reduce ammonia emissions in beef feed lots (Shi et al, 2001).

    - [Note: A significant number of dairy farmers in the US use humic products to reduce ammonia emissions in dairy operations by spreading dry humic substances on livestock manures at a rate of 0.5 lb. /head/day or adding liquid humates to dairy and hog manure slurries at very low inclusion rates effectively reducing odors. The practice is also intended to reduce nitrogen leaching and atmospheric release after field application. There are numerous reports regarding the substantial decline of pneumonia in calving operations that spread dry humates on manures and some dairy operations feed humates *ad libitum* (free choice) to reduce blood urea nitrogen (BUN) in newborn calves.]

- Phosphorus Management

  - Humic substances have the ability to stabilize phosphorus fertilizers (Day, et al, 2000)
  - The ability of humic substances to solubilize and complex with natural minerals, such as rock phosphates, is well documented (Chen, et al, 1999). The solubilization of is primarily through interactions with soil microbes (Burdick, 1965: Banfield and Hamers, 1997; Schnitzer, 1986: Martinez et al, 1984; Tan, 1986).
  - Humic substances keep minerals in soil solution keeping them from precipitating with soil iron and aluminum through complexation reactions (Tan, 1986; Banfield and Hamers, 1997; Schnitzer, 1986), and interactions with other common soil elements, especially the lanthanide elements, which are effective in stabilizing phosphorus in soil systems (Banfield and Hamers, 1997).
  - Both humic acid and fulvic acid fractions are capable of solubilizing immobilized aluminum and iron phosphates into bioavailable forms of phosphates (Lobartini et al, 1998; Levesque and Schnitzer, 1967; Weir and Soper, 1963).

- Toxins

  - Humic substances remove toxic metals from the surrounding environment by forming insoluble aggregated spheres around them (Liu and Huang, 1999), thus detoxifying arsenic, cadmium, and aluminum into forms that are not biologically available.
  - Humic substances are the major components of soil organic matter that deactivate both metal and xenobiotic (pesticide) toxins. As a comprehensive reference on the detoxification of contaminants, see Clapp et al (2001a).
  - Over 50% of the composition of natural humic substances consists of the humin fraction, which has been described as being primarily responsible for the ability of humic substances to bind toxins (Rice, 2001, Clapp et al, 2001a).

- Soil Physico-Chemical Interactions
  - Soil nutrients are retained partly due to soil stabilization by humic substances (Piccolo et al, 1999)
  - Humic substances can improve water holding capacity for better drought resistance and reduction in water usage (Russo and Berlyn, 1990)
  - Good soil structure is influenced by humic substances participating in numerous bridging mechanisms, including water, aluminum, and calcium bridging (Tan, 2003, pp. 250-253.)
  - Humic substances are important components of soil redox systems, transferring, donating, accepting, and shuttling electrons (Tan, 2003, pp. 259-260; Jiang and Kappler, 2008).

- Plant growth stimulants
  - 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, Chen et al, 2004) and worldwide (Karr, 2001)
  - 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)
  - The addition of humic substances to soils, including calcareous soils, can stimulate growth beyond the effects of mineral nutrients alone (Chen, et al, 1999).
  - Humic substances are active soil redox agents can reducing fixed soil iron (Fe^{3+}) to bioavailable iron (Fe^{2+}) (Rakshit et al, 2009)
  - The hormone-like stimulatory effects of humic substances on plant growth has been attributed to the increased uptake of micronutrients (Chen et al, 2004a)
  - The stimulatory effects of humic substances are non-hormonal when tested in nutrient solution (Chen et al, 1994; Clapp et al, 2001). However, there is also evidence that humic substances found in worm excreta have exchangeable auxin groups attached to them (Canellas et al, 2000)

- Microbial Stimulants
  - Humic substances enhance the uptake of minerals through the stimulation of microbiological activity. (Albuzio et al, 1994; Figliolia et al, 1994; Visser, 1985; Nardi, et al, 1996; Paciolla, et al, 1998: Day et al, 2000)
  - Humic substances are capable of stabilizing the metabolic activity of bacterial strains used in bioremediation of contaminants, thus increasing their effectiveness (Hwang and Tate, 1997)
  - Carbon and nitrogen cycling primarily involves microorganisms, having both a direct and indirect effects on nutrient cycling and environmental quality (Muller-Wegener, 1988).
  - Enzyme activity is preserved by humic substances, imparting a high degree of resistance to decomposition and denaturing, allowing enzymes to persist for many years in soils (Jackson, 1995).
  - Humic substances are generally regarded in the scientific community as microbiological stimulants and powerful detoxifying agents (Hudák et al, 1997; Perminova et al, 2001).
  - Humic substances stimulate microbiological activity. (Albuzio et al, 1994; Figliolia et al, 1994; Visser, 1985; Nardi, et al, 1996; Paciolla, et al, 1998: Day et al, 2000)
  - Humic substances are responsible for mediating all soil geomicrobiological and geochemical interactions by providing the media on which complex interactions among soil metals, organic substances and microbes may occur (Huang, 2002).

- Mechanisms
  - Plant growth stimulation by humic substances at extremely low concentrations has been explained as a hormonal-like growth effect by numerous authors (Xunzhong Zhang and Schmidt, 2000; Nardi et al, 2002; Basiolio et al, 2007; Aguirre et al, 2009).
  - One aspect of plant growth stimulation has been attributed to humic acid activation of plasma membrane H^+- ATPase which causes a redistribution of nitrate concentration from root to shoot. Nitrate redistribution triggers the release of cytokinins and polyamines that induce the translocation of plant nutrient minerals (especially K, Mg and sulfur) from the roots to the shoots (Mora et al, 2010; Pinton et al, 1997; Canellas et al., 2002).
  - Quagiotti et al. (2004) demonstrated that humic substances directly effect gene transcription on root genes encoded for H^+-ATPase promoting nitrate influx in roots and nitrate transporters that impact accumulation of nitrates in leaves.
  - Humic substances in the presence of low soil concentrations of potassium cations (K^+) has a stronger stimulatory effect on H^+- ATPase-induced H^+ (acids) efflux into the rhizosphere of oat seedlings than high concentrations of K^+ (Pinton et al, 1997), which is consistent with field studies where low soil nutrient concentration in the presence of humic substances (David et al, 1994; Chen and Aviad, 1990; Chen et al, 2004a) participate in a biological priming effect (DeSwart and Van Diest, 1987) which triggers a cascade of biological events resulting in increased plant nutrient availability when soluble soil nutrients are limited.
  - Chelation and complexation by humic substances keeps plant nutrients in soil solutions (Tan, 1986; Chen, et al, 1999; Clapp, et al, 1998).
  - Reactive species of aluminum (Al^{3+}) inhibit H+-ATPase activity by decreasing the surface charge on the plasma membrane in plants (Ahn et al, 2001). However, aluminum is readily complexed by humic substances resulting in a highly stabilized form of aluminum (Schnitzer, 1978).
  - Humic-metal complexation accounts for a great deal of humic substances' chemical activity. Numerous models have been proposed by many authors, within hundreds of publications, addressing humic-metal complexation. Perdue (2001) presents an overview of the three most successful models.
  - Humic substances interact with a variety of solutes, because of their poly dispersity, polyelectrolyte characteristics, high specific surface area, high surface reactivity, high cation exchange capacity, and photochemical activity. Pre-eminent among the interactions of humic substances with solutes are those involving cations, i.e. H^+, Na^+, Al^{3+}, Ca^{2+}, Cu^{2+}, Pb^{2+}, etc. Cation-humic interactions exert control over the reactivity and bioavailability of soil and water cations. Tipping (2002) provides a comprehensive review of current predictive and mathematical models and their application to the natural environment.
  - The reactivity of humic substances with mineral surfaces was reviewed by Bailey et al (2001) using computational chemistry, scanning probe microscopy and virtual reality for predicting the chemical reactivity of humic substances with xenobiotics (toxins) from the perspective of surface reactivity.
  - Natural humic substances may be complex "supermixture" of high and low molecular weight humic substances (MacCarthy, 2001). The higher molecular weight components (humic acids) also engage in solubilizing minerals and have a high capacity for stimulating biological activity. The chemical reactivity and chelating ability of humic acids is equal to or greater than fulvic acids (Tan, 2003).
  - There is increasing evidence that biological activity of humic substances is related more to their molecular structure than molecular weight (Muscolo et al, 2007).

- Humic substances participate in the rhizosphere interactions coating soil clays as part of soil genesis, weathering, and soil aggregate formation (McKeague et al, 1986).
- Dissolution of insoluble soil minerals by fulvic acids occurs in the presence of microbes at extremely dilute solution concentrations, with iron-containing minerals being the most susceptible to attach by fulvic acids (Schnitzer, 1986).
- Tombacz and Rice (1999) attributed the release of soluble nutrients from minerals to the membrane-like layers of humic substances that form on the mineral surfaces. Humic substances form micelles (Piccolo et al, 1996; Sutton and Sposito, 2005), which are aggregates of amphiphilic molecules having hydrophilic (polar) ends arranged towards the soil solution while their hydrophobic ends arranged towards the center of the aggregate away from the outer solution. This explains, in part, their high surface activity and strong association with soil solution cations (Yates and von Wandruszka, 2005).
- Wang et al, 1995 reported increased uptake of phosphorus and improved yield in a greenhouse and field study on wheat grown on an alkaline soil. They attributed the result to the ability of applied humic acids to prevent fixation of phosphates, thus maintaining phosphorus in soil solution.
- Humic substances effect plant cell membrane permeability, activating respiration, the Krebs cycle, photosynthesis, production of adenosine triphosphate, and amino acids (Malcolm and Vaughn 1978, 1979; Vaughan and Malcolm, 1985)
- Humic substances at low concentration (10 µg of organic carbon mL^{-1}) in deionized water, stimulated the release (efflux) of H+ protons from oat roots, significantly decreasing the water pH, supporting the concept that humic substances either directly or indirectly acidify the rhizosphere, helping to explain why humic substances are used to increase fertilizer efficiency (Pinton et al, 1997).
- Pinton et al, (1999) studied the effect of extracted humic substances on plasma membrane H^+ATPase activity of maize roots, and found significant increases in plasma membrane H^+ATPase activity.
- Humic substances preserve enzymes, substantially extending their persistence and activity in soils (Jackson, 1995). Clay-humic complexes protect enzymes that are released from biological activity, preserving them, particularly when complexed with calcium-montmorillonite clays (Burns, 1986).
- Numerous papers have been published on the ability of humic matter to form stable complexes with urease enzymes. Nitrifying chemo-autotrophs such a *Nitrosomonas* species may be aided by the ability of humic substances to preserve other enzymes, such as asparaginase, amidase, and D-glutaminase, reducing the energy needed by these bacteria to hydrolyze NH_4^+ (Burns, 1986).

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Submitted by: Lawrence Mayhew
March 18, 2011