

## Humic products – potential or presumption for agriculture? Can humic products improve my soil?

KL Billingham

NSW Department of Primary Industries, Taree NSW: kim.billingham@dpi.nsw.gov.au

**Abstract:** *More than 200 humic products are currently being manufactured and sold as soil amendments by Australian companies. Many more are available from overseas suppliers. They are marketed with the promise of enhanced plant growth and improved soil physical, chemical and biological properties. The list of claims closely resembles the properties of humic substances that occur naturally in soils and are responsible for many of its functions. Australian agricultural soils contain from 13 to 21 tonnes/ha of natural humic substances. Sufficient doubt exists as to whether claims can be made for humic products on the basis of their similarity to humic substances in soils. Although mechanisms can be explained for their mode of action and there have been some positive results in laboratory and glasshouse experiments, there is not yet sufficient evidence that humic products will provide a production or environmental advantage in the field. A major problem is that, possibly due to their cost, recommended application rates are set too low to have any positive benefit. Producers are encouraged to conduct their own trials before committing to a major purchase of humic products.*

**Key words:** humic acid, fulvic acid, soil structure, humic-clay complexes, water-holding capacity, amphiphilic properties

### Introduction

Our dominantly urban population in Australia is taking a growing interest in environmental issues, fed by an attentive media. This same population is becoming increasingly divorced from agriculture, which is often blamed for soil and water degradation. Alternative philosophies propose ‘chemical-free’ farming methods and a range of products are emerging, promoted as answers for sustainable agriculture.

Amongst these, humic products are gaining a commercial niche. More than 200 humic products are currently manufactured and sold by Australian companies (Billingham 2012). Many more can be purchased *via* overseas websites. They are marketed with a myriad of claims of improved physical, chemical and biological soil properties and enhanced plant growth. These humic products might variously:

- Promote good soil structure;
- Increase water holding and cation exchange capacities;
- Stabilise nitrogen, phosphorus, calcium and micronutrients whilst improving their uptake by plants;

- Buffer against soil acidity and salinity;
- Regulate plant growth;
- Stimulate germination and root and shoot growth;
- Improve yield, and
- Increase plant resistance to drought, disease and other stress factors.

Are these claims too good to be true or is there a potential role for humic products in Australian agriculture, especially the grazing industries? What do we know about these products? How do they work? Is there sufficient evidence to support the claims or are they simply a presumption on the part of manufacturers? The author (Billingham 2012) recently surveyed information from the websites of 15 Australian companies marketing humic products for broadacre cropping and pasture production. The advertised claims were examined in the light of the existing peer-reviewed literature. As very little research into humic products has been conducted in Australia the review was extended world-wide.

### What are humic products?

The term ‘humic products’ denotes a range of materials derived from lignites (brown coals), peats, lignins, composts and other organic

wastes. Leonardite, a type of brown coal rich in humic acids, the active ingredient (Dailey 1999), is a popular source. Most humic products are manufactured by alkali extraction of the source material with sodium, potassium or ammonium hydroxides (Perminova and Hatfield 2005), then precipitated with an acid to produce the solid range of products.

Humic products are usually sold as soil amendments under a wide range of trade names and product descriptions (Billingham 2012). The market is unregulated and there are no standardisation requirements. Common groupings are:

- The humic acids and humates, which are usually sold in a powdered, granular or pelletised form;
- The fulvic acids and fulvates, which are often marketed as liquid foliar sprays, and
- Natural, organic or 'raw' humates, which have not been extracted with an alkali.

There are many other product names such as humalite and slack lignite and the archaic term, 'ulmic acid' (Mayhew 2004).

Although rarely advertised as a complete fertiliser replacement (Billingham 2012), humic products are often blended with macro and/or micronutrients with the broad claim of increasing the efficiency of fertiliser use. Most application rates range from 5 kg/ha to 1 t/ha for solid products and 1–50 L/ha for liquid products with dilution rates up to 1:200. Available prices in 2012 ranged from \$35 per 5 L drum to more than \$2500/t (Billingham 2012).

It is the use of the terms humic and fulvic acids and their salts, the humates and fulvates, that gives manufacturers their best marketing advantage. They are aligning their products with naturally occurring humic substances, which make up a large proportion of soil organic matter (SOM). Humic substances provide the structural and functional properties of soil that have been more broadly attributed to SOM (Ghabbour and Davies 2001; MacCarthy *et al.* 1990; Perminova *et al.* 2005; Stevenson 1994).

## What are humic substances?

Humic substances constitute the stable fraction of soil organic carbon that resists microbial degradation. They are extremely complex, randomly structured macromolecules or supermolecules (Huang and Hardie 2009) and are ubiquitous in nature, being found wherever organic matter has decayed: in soils, sediments, water, peat bogs, carbonaceous shales, lignites and sewage. Humic substances account for 50 to 80% of the organic carbon in soils (Piccolo 2001; Rice 2001). Assuming an average bulk density of 1.3 g/cm<sup>3</sup> and an organic carbon level of 2% (Chan *et al.* 2010), Australian agricultural soils would have between 13 to 21 tonnes (t)/ha of humic substances in the top 0.1 m. Pasture soils would be at the higher end of this range as they store more carbon than cropped soils (Chan *et al.* 2010).

Despite decades of research, the nature of humic substances is not well understood. Their formation by the process of humification, their structure and how they work in soils are still the subjects of research and debate with a number of models under investigation (Tate 2001). What is known is that humic substances are able to carry out a number of vital soil functions because they are both highly chemically reactive and yet very recalcitrant or refractory. That is, they resist microbial degradation due to their complexity and extremely random structure (MacCarthy 2001a) and their ability to form complexes with soil minerals (Huang and Hardie 2009). Other organic compounds, such as polysaccharides and proteins, are also chemically active but do not survive long enough in soils to maintain the following essential physical, chemical and biological functions:

- Formation of organo-clay complexes and resulting stable soil aggregates;
- Improvement of water holding capacity;
- Soil temperature regulation;
- Electrochemical and ion exchange properties;
- Formation of colloids;
- Complexation of metal ions with accompanying chelation reactions;

- Adsorption of organic chemicals including pesticides;
- Control of plant pathogens, and
- Hormone-like activity in plant growth.

It is very difficult to extract intact humic material from the mineral component of soils (Tan *et al.* 1992). Much of the research into humic substances has been done by extracting three humic fractions from soils with alkaline solutions:

- Humic acids – are soluble at pH values above 2 and precipitate out below pH 2;
- Fulvic acids – are soluble in water at all pH values, and
- Humin – is not soluble in water at any pH value.

A number of other analytical methods, such as electron microscopy and diffraction and a variety of spectrometry and nuclear magnetic resonance techniques are being investigated to assist in the study of humic substances (Balsler 2005).

From this research substantial evidence has been gathered about the chemical reactivity of humic substances. It is due to the large number of oxygen and nitrogen functional groups attached to the molecular superstructure (MacCarthy 2001b). The most important are the carboxyl and phenolic oxygen functional groups. They are acidic, donating protons ( $H^+$  ions) into the soil solution and leaving a number of negatively charged sites on the humic molecule that can react with water, plant nutrients and clay minerals in soil aggregates (Figure 1).

Another theory of humic structure, for which evidence is mounting, is that humic molecules are amphiphilic in nature (Piccolo 2001; Wershaw 1986). Amphiphiles, for example detergents, have a hydrophilic (water-loving) part that attracts water and a hydrophobic (water-fearing) part that repels water (Figure 2). Because of this amphiphilic property, humic molecules can aggregate into micelles (droplets) or form membranes. They can also react with a wide range of organic molecules.

### Are humic products the same as humic substances?

There is a remarkable similarity between the claims made about humic products and the well-established properties of humic substances. Certainly, manufacturers use similar methods as researchers to extract humic and fulvic acids. Are there enough similarities between them to make claims about humic products based on the properties of naturally occurring humic substances?

Products manufactured from the brown coals, lignites and leonardites, as well as peats do contain varying proportions of humic substances (Hayes and Clapp 2001). However, products sourced from composts and lignins have not undergone the biological transformations inherent in the humification process. Treating an organic material with alkali and acid may produce something that looks like a humate, but it may not behave like one.

To function effectively in soils humic materials need to be recalcitrant and resist microbial degradation. The average age of naturally occurring humic substances has been measured

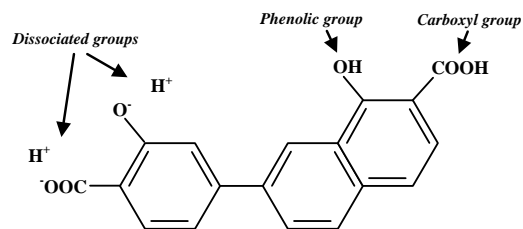


Figure 1. Portion of a hypothetical humic molecule with carboxyl and phenolic groups in their undissociated and dissociated forms.

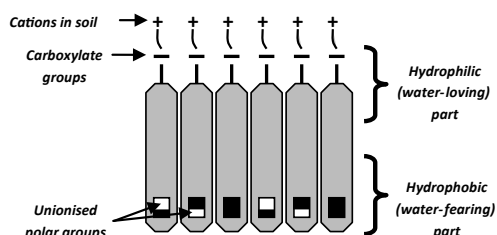


Figure 2. Membrane-like humic aggregate showing its amphiphilic nature with a hydrophobic part at the non-polar end and a highly charged hydrophilic part at the polar end.

from months to thousands of years (Kastner and Hofrichter 2001; Stevenson 1994). Stott and Martin (1990) calculated that new humic material decomposes at a faster rate than old. Can humic products survive microbial attack and decomposition long enough to carry out the many functions for which they were applied?

There is also an issue of product quality. If quality refers to the percentage of humic and/or fulvic acids in a product, there is a wide variation due to differing source materials and manufacturing processes. The method of analysis can also affect the result. In a survey of ten commercial humic products, Fataftah *et al.* (2001) found that, depending on the analytical method used, the humic acid content varied from that advertised by more than 800%.

A fourth problem lies in the extraction and isolation of humic and fulvic acids themselves, whether from soils or in the manufacture of humic products. Feller (1997) has suggested that these extracted fractions may simply be the result of the denaturation of the original humic compounds and may not even exist in soils. They might not actually be relevant in soil processes (Hayes and Clapp 2001).

There is sufficient doubt to suggest that companies selling humic products cannot reasonably promote them solely on the basis of their similarity to humic substances that occur naturally in soils. Claims of physical, chemical and biological benefits must stand on their own in the light of independent field trials and data.

### **Can humic products improve my soil?**

The most obvious question that must be asked is – if Australian pasture soils already contain upwards of 17 t/ha of natural humic substances, why buy and add any more? The first commercial humic products appeared in the 1950s and 1960s when research was demonstrating the potential of humic amendments (Kline and Wilson 1994). They were marketed aggressively with many miraculous claims. When these were not realised in the field, mistrust of humic products grew in both the agricultural and research communities.

Early promising results were ignored and research moved in other directions (Kline and

Wilson 1994), including studies into humic substances extracted from soils. However, a limited body of scientific literature was gathered through which commercial humic products have been tested for chemical, physical and biological properties. Extracting humic substances from soils is a time-consuming and costly business. Some researchers turned to commercial humic products to ease the strain on staff and budgets, despite warnings about the relevance of any positive results (Malcolm and MacCarthy 1986). A lack of information about the origins, extraction and pre-treatment methods of commercial products and the geochemical and environmental significance of data obtained from them were the main concerns.

Most research into humic products has taken place in the laboratory and glasshouse. Very few field trials have been conducted across the world and most of those tested the effect of humic products on horticultural crops. Billingham (2012) reviewed 20 studies that examined the effect of humic products on plant growth. Three were laboratory trials and four were conducted in hydroponic solution. Only six of the nine pot trials used soil. The four field trials encompassed a range of crops, soil types, environments, products and application rates with no repeatability. A one-off positive response for a particular product applied to a crop in a certain environment may be due to random variation and might, just as easily, have been a negative response.

With these limitations in mind we will look at two physical soil properties asking:

1. Given our current understanding of the mechanisms underlying soil physical properties, can we explain how humic products work?
2. Is there sufficient evidence from independent trials that the products will work under field conditions?

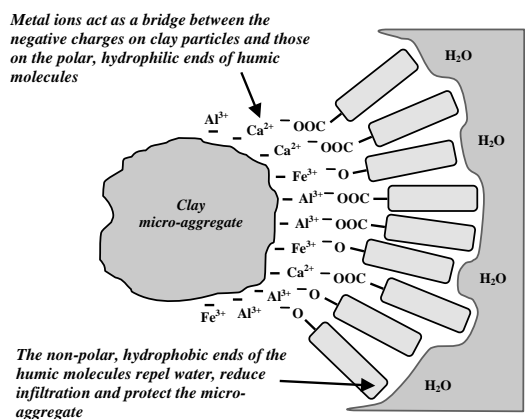
### **Soil structure**

The loss of organic matter from soil and the accompanying decline of soil structure is a concern across the world. In Australia, overgrazing and pasturing hard-hoofed

animals on wet soil has resulted in erosion, soil compaction and structural decline. Researchers have trialled commercial humic products as soil conditioners that might improve aggregate stability. Manufacturers are quick to point out the merits of their products in relation to soil structure.

The mechanisms by which both natural humic substances and commercial humic products stabilise soil aggregates are not yet well understood. Several types of electrochemical bonds may be involved (Stevenson 1994). A commonly accepted explanation is that humic molecules form complexes with clays *via* metal cations that act as a bridge, or chelate, between the two (Figure 3). Positively charged ions such as aluminium ( $\text{Al}^{3+}$ ), iron ( $\text{Fe}^{2+}$ ) and calcium ( $\text{Ca}^{2+}$ ) form bonds with both the negative charges on clay micro-aggregates and the hydrophilic, negative ends of humic molecules where carboxyl and phenolic groups have dissociated. As the clays attract the polar, charged ends of the humic molecules, which aggregate into a clump, the non-polar ends are left sticking out into the surrounding soil water. These hydrophobic ends repel water molecules, forming a water-repellent exterior around the micro-aggregate. With water infiltration reduced the micro-aggregate is better protected and thus stabilised.

A number of laboratory studies, including some conducted in Australia, have shown that humic acids (HA) have the potential to improve soil



**Figure 3.** Conceptual diagram of complexes that can form between humic molecules and clay particles, protecting the structure of micro-aggregates.

stability. Application rates as low as 100 kg HA/ha of a commercial potassium humate increased the mean-weight diameter of aggregates from an acid soil in the Yarra Valley, Victoria (Imbufe *et al.* 2005). However, the same study showed that a sodic soil from the Goulburn Valley, Victoria required 2 t HA/ha to significantly improve its structure. Yamaguchi *et al.* (2004) compared the effects of calcium additions with humic acids derived from lignite and peat on sodic West Australian soils. Although the humic acids could not form micro-aggregates in a kaolin-quartz mix, the lignite-derived HA amplified the effect by 30% of micro-aggregates formed initially with calcium. Peat-HA was more effective than lignite-HA in aggregating the sodic wheatbelt soils in acid conditions.

Overseas, Piccolo *et al.* (1996; 1997b) showed that low application rates of humic acids at 100 to 200 kg HA/ha improved the aggregate stability of severely degraded Mediterranean soils by up to 120% and reduced the disaggregating effects of wet/dry cycles. Piccolo and Mbagwu (1999) removed the native organic matter from an agricultural soil to compare the action of amendments on soils with and without organic matter. Humic acid applied at 400 kg HA/ha increased aggregate stability by 27% in the soil without organic matter and by 73% in the soil with organic matter. To investigate the stabilising effects of humic acids under rainfall, Piccolo *et al.* (1997a) conducted a rainfall simulation trial with a severely compacted loam and a low porosity, dispersing silty loam with salinity and crusting problems. With the simulator providing 40 mm rainfall/hour, soil loss was reduced by 36% on the silty loam with an application of 100 kg HA/ha and on the loam with 200 kg HA/ha. The delay in runoff initiation and accelerated drainage contributed up to 81% of the reduction in erosion.

With promising data from laboratory and rainfall simulation experiments and a mechanism to support the results, the next logical step should be to test the effect of humic acids on soil structure in the field. However, in an extensive review of the literature, Billingham (2012) found only one trial on the subject. In a five-year study of organic amendments, Albiach

*et al.* (2001) found that a commercial humic acid solution applied to a sandy-silty loam at the recommended rate of 100 L HA/ha/year had no significant effect on the parameters tested: organic matter, total humic substances, humic acids, carbohydrates or microbial gums. They concluded that, due to the high cost of the commercial humic acid, the manufacturers had set the application at unrealistically low rates to attract sales.

Most of the manufacturers surveyed by Billingham (2012) set their application rates for humic products well below those that have achieved significant results in laboratory studies. Until independent field trials are carried out at rates that have been shown to be beneficial and cost-benefit comparisons made with other amendments, humic products cannot be recommended for the improvement of soil structure. Any small, incremental changes that may accrue from the lower, recommended rates will need to be measured in long-term studies.

### Water holding capacity

It stands to reason that, if humic products can improve soil structure, then they should have an effect on soil water properties. Improved soil stability and the formation of soil aggregates should increase porosity and, hence, water holding capacity. Despite the ease with which soil water content can be measured, few studies have been done on the association of humic products and soil moisture availability (Van Dyke 2008).

During their studies into soil structure, Piccolo *et al.* (1996) measured the effect of a coal-derived humic acid on three severely degraded Mediterranean agricultural soils. At 100 kg HA/ha available water capacity was increased by an average of 22% across the three soils. In their rainfall simulator study, Piccolo *et al.* (1997a) attributed the reduction in run-off erosion, with humic acids applied at 100 kg HA/ha, more to improved water retention capacity than to aggregate stability. However, when Van Dyke (2008) applied humic acids at commercial rates to putting greens, the treatment reduced the volumetric water content significantly and dried down the root zone.

It appears that humic molecules have the capacity to both attract and repel water. This is due to their amphiphilic nature, having both hydrophilic and hydrophobic parts. When humic and fulvic acids are added to the soil solution they can act as colloids (Stevenson 1994). That is, they aggregate into micelles or droplets suspended in the soil solution (Figure 4). The hydrophobic (water-fearing) parts hide in the centre of the micelle with the hydrophilic, 'water-loving' parts facing out into and attracting and holding water (Wershaw 1986).

However, if the humic and fulvic acids form humic-clay complexes, they will organise into a film with the hydrophilic parts bonded to the clay surfaces *via* cation chelates, or bridges (Figure 3). This leaves the hydrophobic parts exposed to the soil solution. Water molecules are repelled from the clay micro-aggregates, potentially decreasing the wettability and water-holding capacity of the soil.

The problem is that we do not know which soil conditions will cause humic and fulvic acids to form colloids or humic-clay complexes. Stevenson (1994) has suggested that the pH, ionic concentration and presence of neutral salts all have a role to play. The laboratory and field work simply has not yet been done. Until more data is available it would not be prudent to recommend humic products on their ability to improve water retention in soils. Also, given the wide variation in chemical analyses of humic products, each one would need to be tested in a variety of soil types

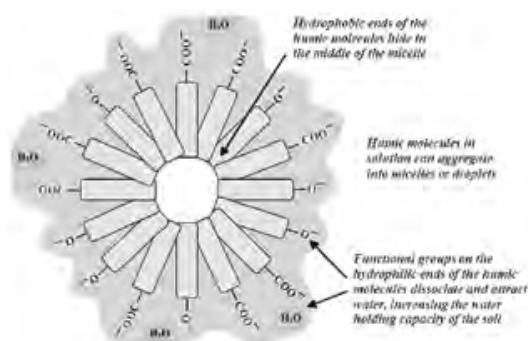


Figure 4. Conceptual diagram of a humic micelle with the hydrophobic ends hidden in the interior and the hydrophilic ends attracting and holding water molecules.

and conditions before claims of improved water holding capacity could be made.

### **What about other soil properties?**

Billingham (2012) has provided a comprehensive literature review of the evidence relating to humic products and soil properties and their underlying mechanisms. Again, most of the research has been done in laboratories and glasshouses. The number of field trials is very small and few have been conducted in Australia or on pasture soils. In terms of the potential of humic products for plant growth and yield, nutrient availability, possibilities for soil remediation and biological effects, Billingham (2012) concluded:

- Plant growth and yield – Positive germination responses have been observed in laboratory and pot experiments. Foliar and soil applications have resulted in increased seedling growth, especially that of roots. In the field, there have been yield increases in grapes, olives and potatoes.
- Nitrogen (N) – The N bound into humic molecules or added during manufacturing processes is largely unavailable to plants. There have been mixed results from coating or mixing urea with humates. Any effect on microorganisms and enzyme activity has not been established. Some positive results have come from the synergistic effect of humic material on N uptake by plants.
- Phosphorus (P) – Humic and fulvic acids can increase P availability in both calcareous alkaline soils and acid soils with high levels of aluminium and/or iron. However, there have been mixed results with crop yields. Care should be taken when using these products on soils with high available P due to the potential increase of P transport through the profile and into waterways.
- Cation exchange capacity (CEC) – Virtually no studies have been conducted on the effect of humic products on CEC. Companies rely on the well-established correlation between the organic matter content of soils and CEC.
- pH buffering – The ability of humic substances to buffer soils is well established and, once again, the commercial products rely on this fact. However, it is not possible to predict how a certain quantity of a particular product will affect the pH of a given soil. There are competing chemical reactions for the available functional sites on the humic molecules and the trial work relating to pH has not been done.
- Micronutrient availability – There is sufficient evidence for the role of humic molecules in the sorption of metal ions and their transport to and into plant roots. However, if a humate can pick up and carry a trace element to a root, it can carry a toxic heavy metal as well.
- Soil remediation – The role of humic substances and products in the remediation of both heavy metals and organic pollutants in the soil has been well established. There is great potential, but the activity of humic molecules in any situation can not be predicted. Researchers are currently working on ‘designer humics’ to carry out specific tasks, and
- Biological effects – Although the direct effect of humic products on plant growth has been established in the laboratory, the mechanism is not yet known. Researchers are working on a possible hormone-like effect and the improved uptake of micronutrients.

### **Conclusions**

Humic products do show some potential for agriculture. However, sufficient field evidence does not yet exist to recommend them for cropping or pasture systems. Given the volume of humic substances that already occur naturally in many pasture soils and the low application rates recommended for humic products, any presumed additional benefit should be questioned. Producers who are interested in humic products are advised to carry out their own small-scale field trials, including a cost-benefit comparison with other amendments, before committing their pockets, pastures and production systems to a broader application of humic products.

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