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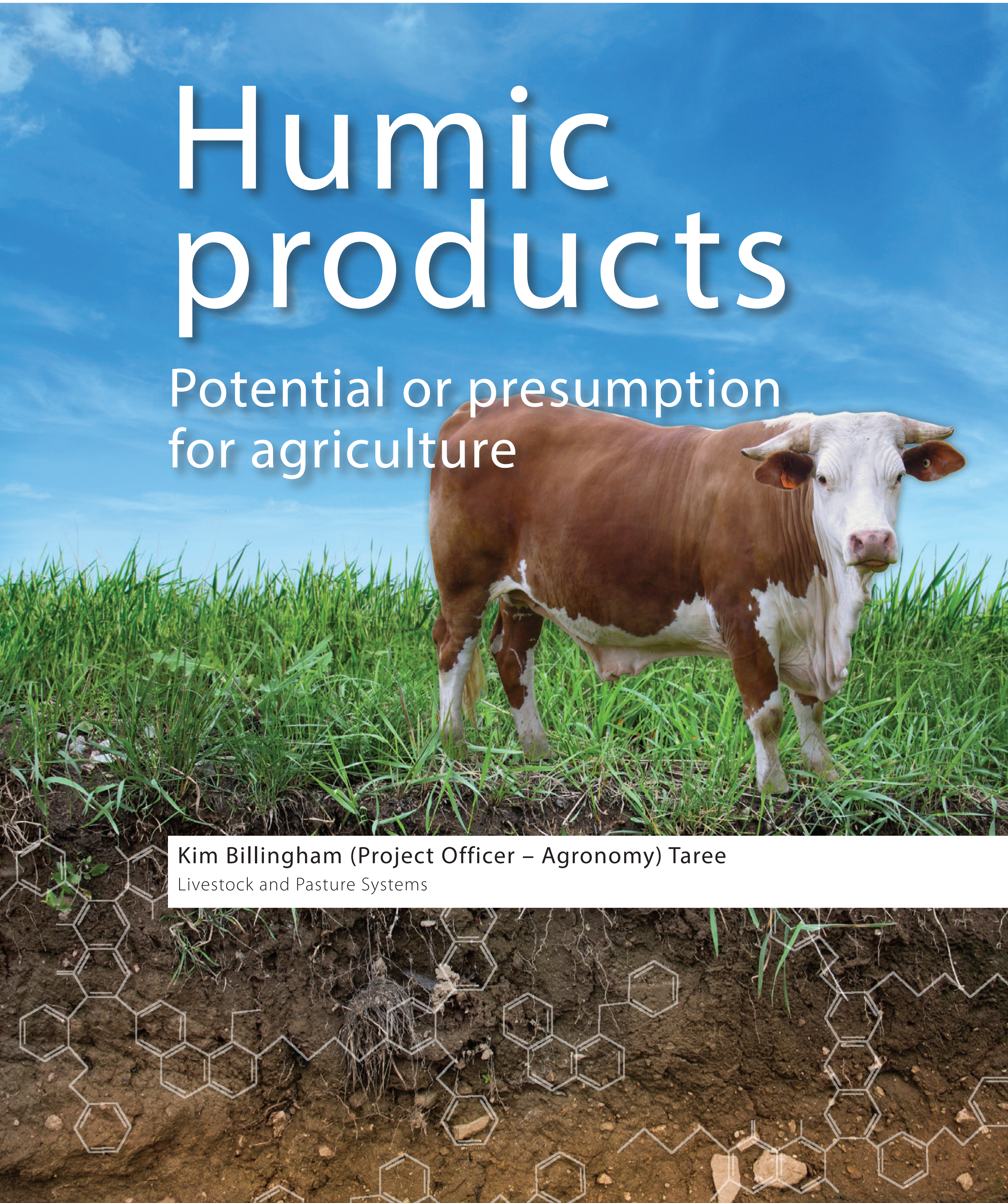

Humic products

Potential or presumption for agriculture

Kim Billingham (Project Officer – Agronomy) Taree
Livestock and Pasture Systems

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Livestock and Pasture Systems, July 2012

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Foreword

A range of products, often referred to as alternative fertilisers, are marketed with numerous claims relating to soil health and improved plant growth. However, there is often an absence of evidence about the veracity of the claims and the effectiveness of these products. Producers and consumers alike are left to rely on the advertised promises which come with little proof.

One common group of alternative fertilisers are the humic products that are often sold as soil amendments with or without accompanying plant nutrients. More than 200 humic products are currently manufactured and sold in Australia. Thousands more are available for purchase via overseas websites. Is there a place for humic products in Australian agriculture? Do they have the potential to realise at least some of the advertised claims or are these benefits merely presumption on the part of manufacturers?

This technical bulletin 'Humic products – Potential or presumption for agriculture' is the first in a series that will cover a range of alternative fertiliser products. Written and produced by NSW Department of Primary Industries, these reports ask two basic questions:

- Can the product work? Given our current understanding of the physical, chemical and biological mechanisms that interact in soil-plant ecosystems, can we explain how the product functions?
- Does the product work? Is there sufficient evidence from independent trials that the product will work under field conditions?

This publication is written primarily for agronomists, soil scientists, consultants and other farm advisors. However, the readable style, explanations and diagrams provided by the author, Kim Billingham, make it accessible for others with a more rudimentary understanding of the soil and plant sciences. 'A brief history of humus' will engage readers from both conventional and more alternative philosophies as we all work towards farming in a more sustainable manner.

Peter Orchard

Manager, Pasture R, D & E

NSW DPI

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Abbreviations, Symbols and Units

ACA	Australian Coal Association
Al	Aluminium
Amu	Atomic mass unit
ATP	Adenosine triphosphate
ADP	Adenosine diphosphate
BFA	Biological Farmers of Australia
Br	Bromine
C	Carbon
Ca	Calcium
Cd	Cadmium
CEC	Cation exchange capacity
Cl	Chlorine
cm	Centimetre
cmol	Centimole
Cu	Copper
Da	Dalton
DNA	Deoxyribonucleic acid
DOC	Dissolved organic carbon
EDTA	Ethylenediaminetetraacetic acid
ESR	Electron spin resonance
F	Fluorine
FA	Fulvic acid
Fe	Iron
g	Gram
H	Hydrogen
ha	Hectare
HA	Humic acid
HAP	Hydroxyapatite
Hg	Mercury
HS	Humic substance
HUN	Hydrolysable unknown-N
IAA	Indole-3-acetic acid
IFOAM	International Federation of Organic Agricultural Movements
IHSS	International Humic Substances Society
IR	Infrared
K	Potassium
kg	Kilogram
L	Litre
Li	Lithium
lb	Pound
µg	Microgram
m	Metre
MAP	Monoammonium phosphate
meq	Milliequivalent
mg	Milligram
Mg	Magnesium
mm	Millimetre
mmol	Millimole
MO	Microorganism
MS	Mass spectrometry
MSDS	Material Safety Data Sheet
MWD	Mean-weight diameter
N	Nitrogen
Na	Sodium
NASAA	National Association for Sustainable Agriculture, Australia
NATO	North Atlantic Treaty Organisation
NEC	Nitrogen-enriched coal
Ni	Nickel
nm	Nanometre
NMR	Nuclear magnetic resonance
NOM	Non-living natural organic matter
O	Oxygen
OMRI	Organic Materials Review Institute
P	Phosphorus
PAH	Polycyclic aromatic hydrocarbon
Pb	Lead
PCB	Polychlorinated biphenyl
ppm	Parts per million
RNA	Ribonucleic acid
S	Sulphur
SOM	Soil organic matter
Sr	Strontium
ssp.	Species
t	Tonne
USA	United States of America
USDA	United States Department of Agriculture
UV	Ultraviolet
Zn	Zinc

EXECUTIVE SUMMARY

Humic substances are complex organic molecules that occur naturally in soils, sediments and water. They also make up a large proportion of the organic matter in peats and brown coals. Humic products are manufactured from brown coals, peats, composts and other organic material.

Manufacturers and resellers of humic products make a number of claims about the physical, chemical and biological properties of their merchandise. This report evaluates these claims against the evidence found in the peer-reviewed literature. The nature and characteristics of humic substances that occur naturally in soils are explored to provide a scientific basis for the comparison. Information from the websites of 15 Australian companies, marketing humic products for broadacre cropping and pasture production, is analysed and the claims investigated. In addition, a brief history of the role of humus in agriculture throughout the centuries is included.

A brief history of humus

The role of humus in soils has been acknowledged since ancient times as it provided the 'fat of the land'. From the writings of the Romans to the early 20th century there has been a constant struggle to find sufficient organic matter, in the form of manures and composts, to build and maintain the quality of agricultural soils. There was never enough manure and, over time, the soils were exhausted. Limestone, sedimentary chalks and marls, sea sand, pond mud and the ashes from dried, burnt tussocks and other plants were all used as soil amendments where they were available.

For nearly 2000 years until the mid-1800s, scientific thinking was dominated by the teachings of Aristotle and there were few advances in the plant sciences. As observation and experimentation gradually replaced dogma, new discoveries were made and theories were promoted, some to be later discarded. Humus Theory was largely accepted by scientists and agriculturalists before 1840. Plants obtained their food by absorbing soluble humus from the soil via their roots and assimilating it into their tissues.

By the mid-1800s the role of photosynthesis in plant nutrition was being unravelled. Sprengel and Liebig in Germany and Lawes and Gilbert in England established that plants required a number of minerals that they absorbed from the soil. These plant nutrients could be supplied from mineral fertilisers. The Mineralist Theory slowly replaced Humus Theory and the search for commercial sources of fertilisers began. In regions where the new fertilisers were used more food was being grown than could be consumed. Fertiliser use in the 20th century resulted in whole populations being free from hunger for the first time in history.

Despite this, during the 1900s public concerns were raised about the sustainability of intensive agriculture, especially where soils were being continuously cropped without inputs of organic matter. Alternative agricultural philosophies and methods, including biodynamic and organic farming, were developed and established. The importance of humus, under its new title of soil organic matter, and its role in several soil properties was established during this Ecological Period.

Humic substances

Humic substances are extremely complex super-molecules with random structures. They are ubiquitous in nature, being formed naturally by the breakdown of organic matter during the process of humification. Humic substances are both highly chemically reactive yet recalcitrant, resisting microbial decay. Their role in a number of physical, chemical and biological properties of soils has been well established. Australian agricultural soils contain from 13 to 21 t/ha of humic substances in the top ten centimetres.

Despite a large research effort over several decades, the formation, structure and function of humic substances are not well understood. It is very difficult to extract intact humic substances from soils where they are bound to mineral surfaces. Three fractions can be extracted – humic acid, fulvic acid and humin. Because of the expense and time involved with these extractions, many researchers use commercial humic products in their investigations. This has provided a growing body of research into the potential properties of these products.

Humic products

Humic products are usually sold as soil amendments, often blended with plant nutrients. They are sourced from brown coals, peats and composts from which they are extracted by treatment with alkali and acid. Humic products are sold under a wide variety of trade names and descriptions in an unregulated market with no registration or standardisation requirements. Most recommended application rates range from 5 kg to 1 t/ha, equivalent to 0.03% to 6% of the humic substances occurring naturally in soils. Prices range from $35 per 5 L drum to more than $2,500/t.

The claims made for humic products are based largely on the properties of naturally occurring humic substances. Most studies have been done in laboratories and glasshouses in a variety of mediums. Those using washed sand or a soil-less bedding medium showed a significant increase in shoot and/or root growth. However, the results of pot trials using soil have been inconclusive. Very few field trials have been conducted across the world. Those field trials that have been reported cover a wide variety of soil types, crops, products, application rates and methods with no repeatability. Company websites provide little trial-based evidence.

A number of questions arise relating to humic products:

- Are all humic products humic substances?
  Brown coals do contain varying proportions of humic substances. However, treating an organic waste with alkali and acid may produce a material that looks like a humate but may not behave like one.
- Are humic products recalcitrant in soils?
  There is no information about the retention of these products in soils. As extracted fractions, they may be more degradable than entire humic molecules.
- Are the recommended application rates adequate?
  Given the amounts of naturally occurring humic substances in soils, the relatively low application rates may have a negligible effect.
- Is there any guarantee of product quality?
  The wide range of sources and processing methods results in a substantial variation in product quality, even between different batches of the same product.

Claims of humic products

Individual claims purported by manufacturers of humic products have been evaluated against the scientific literature. Most of the products tested contained humic and/or fulvic acids or salts.

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.

Soil structure

Laboratory and rainfall simulator studies have shown that humic products may have a role in improving soil structure and reducing erosion potential. However, at the low application rates recommended by many companies, there have been no significant results in the field.

Water holding capacity

Depending on how humic molecules aggregate or react with the mineral component of soils, they have the capacity to either attract or repel water. The soil conditions under which each scenario is likely to occur have not yet been established.

Nutrient availability

Nitrogen – The nitrogen 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 – Humic and fulvic acids can increase phosphorus 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 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 simply 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.

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.

Conclusion and recommendations

Humic products show some potential for agriculture, especially in terms of phosphorus and micronutrient availability and soil remediation. However, no recommendations for their use can be made until extensive field trials are conducted and the humic products are compared with other soil amendments with accompanying cost-benefit analyses.

INTRODUCTION

We live at a time when environmental issues are at the forefront of media attention and are of increasing importance to a largely urban population. Much has been said about the perceived detrimental effects of conventional agriculture on the environment. Some alternative philosophies propose a solution based on increasing soil organic matter in chemical-free farming systems. There is a growing awareness amongst farmers of the importance of organic matter in soil health and quality and the potential for soil carbon sequestration.

The fortunes of soil organic matter and its importance to agriculture have waxed and waned throughout the last three centuries. That elusive substance humus, once central to theories of plant nutrition, was relegated to obscurity for almost one hundred years, only to emerge again recently as a potential solution to several environmental problems.

It is now widely accepted that soil organic matter, the modern name for humus, is fundamental to the soil ecosystem, providing physical, chemical and biological benefits. Humic substances, the fraction that is resistant to microbial degradation, comprise up to 70 to 80 percent of the organic carbon in mineral soils (Piccolo 2001) and are largely responsible for its many functions.

Although much is known about the role of humic substances, their mode of action is far from certain (Tate 2001). The search for an understanding of the components, structure and formation of humic substances has become something of a holy grail for soil chemists. As modern analytical procedures have developed, experimental findings have posed more questions than they have answered. Traditional models of humic substances are being questioned and replaced with new concepts.

With the rise of new farming systems and the proliferation of alternatives to conventional inorganic fertilisers, humic products have found a commercial niche. Whereas humic substances occur naturally in soils, humic products are manufactured from brown coals, peats, composts and other organic matter. Many claims are made about their efficacy with some companies promoting their particular humic products as a "cure-all" for agriculture.

Farmers and their advisors are left wondering about the validity of these claims. Is the information provided in brochures and on commercial websites about humic products reliable or, at least, does it reflect current scientific understanding? Have independent trials been conducted to verify the purported claims? If the soil already contains a proportion of humic substances, will adding more achieve anything?

An understanding of humic substances that occur naturally in soils is vital if the information surrounding commercially sold humic products is to be unravelled. Four questions will be posed in this report.

1. What are humic substances and how do they work?
2. What are humic products and what types are currently available on the market?
3. What evidence is available that substantiates the many claims made for the humic products?
4. Does the addition of commercial humic products provide any agronomic or environmental benefits? If so, is their use cost effective?

A fifth question, the role of soil organic matter and humic materials in soil carbon sequestration, is currently the subject of many studies and will not be dealt with in any great depth in this paper. Himes (1998), Swift (2001), Janzen (2006) and Marschner *et al.* (2008) have provided informative reviews on the subject.

Of course, no discussion of humic materials would be possible without regular mention of facets of organic chemistry. An expanded glossary is provided to unravel the language of organic chemistry where explanations provided in the main text do not suffice.

1. A BRIEF HISTORY OF HUMUS

The existence of humus has been known since ancient times. The Romans coined the term 'humus', meaning soil or earth (Feller 1997). Roman writers produced textbooks on farming which included simple forms of soil classification and the correct use of manures (Fussell 1971). They provided advice on how and where to build a dung heap with subsequent application rates and timing for the mature dung. Animal manures, including human ordure, were ranked depending on the intended crop or pasture. Pigeon droppings were considered the most valuable manure with hog dung coming in last.

The term 'humus' was replaced by 'terra' in the 1st century BC, after which humus disappeared from the literature for almost 1,800 years (Feller 1997). The concept, however, was not lost. It was the 'oil', the 'tar' or the 'mucilage' produced by the putrefaction of animal and vegetable remains that provided the food for plants (Fussell 1971). Lime dissolved the 'fatness' of the mucilage or humus and clays fixed and retained this fatness(Waksman 1936). Hence the expression, 'the fat of the land'.

The ancient Greeks, Gauls and Britons had dug up deposits of limestone, nitre [potassium or sodium nitrates] and fine-grained sedimentary clays and chalks, called marl (Fussell 1971). These amendments, spread over fields, were known to improve soil texture and increase crop yields for several years. Sea sand was also dug up and carted to nearby fields, especially if it contained a good proportion of shells.

For nearly 2,000 years, until the mid 18th century, scientific endeavour was dominated by the four elements of Aristotelian philosophy – earth, air, fire and water. There were few advances in plant sciences. Plants absorbed organic matter from the soil via their roots and needed a continuous supply of this food (Fussell 1971). The original thinkers who preferred observation and experimentation to dogma had no other reasoning than that of Aristotle to explain their findings. Their conclusions were often erroneous and progress was slow.

Increasing populations and the intensification of farming systems to meet the demand for food drove the need for a better explanation of plant nutrition. By the 1700s Hale had demonstrated transpiration in plants, Jethro Tull was recommending frequent ploughing to produce a fine tilth and farming textbooks were promoting the importance of 'salts' for plant growth (Fussell 1971). However, these advances were of little use to the average farmer who, being illiterate or having little access to books, continued to farm in the traditional, centuries-old manner.

Figure 1 – Roman marble bust of Aristotle copied from the original Greek bronze by Lysippos (330 BC)

There was a constant struggle to find sufficient manure. Lords of the manor monopolised the supply, 'folding' all the sheep and cattle on their own fields and collecting manure from village markets and fairs. The problem was compounded in regions where firewood was in short supply as dung was burnt for heating and cooking. Where available, limestone, marl or pond mud were dug and spread on arable land. Tussock was cut, dried and burnt and the ashes spread back on the fields. Some entrepreneurs attempted to manufacture fertilisers from soot, ash, unslaked lime, salt and saltpetre (Fussell 1971).

It was during the 1700s that the term 'humus' reappeared in European literature meaning 'loam' or 'mould' (Feller 1997). Linnaeus used 'humus' in a soil classification system similar to the one he developed for plants (Waksman 1936). From the early 1800s humus became the subject of debate amongst agronomists, soil scientists and chemists. Its fortunes underwent a rollercoaster ride for the next 200 years. Once central to theories of plant nutrition, humus was relegated to obscurity for more than 100 years only to emerge again as a potential solution to several environmental problems. Manlay *et al*. (2007) divided this period into three: the Humic Period [before 1840]; the Mineralist Period [1840 – 1940]; and the Ecological Period [1940 – 2000].

The Humic Period [before 1840]

By the turn of the 19th century the shackles of Aristotelian philosophy were finally being thrown off. The process of photosynthesis had been discovered and experiments conducted showing that the greater proportion of plant dry matter came from water and air, not the soil itself (Fussell 1971). These findings were disputed by scientists who promoted humus theory, the assimilation of soluble humus by plant roots, or chemical heterotrophy as we know it today (Manlay *et al*. 2007).

Chief amongst the humus advocates was Albrecht Thaer, a German agronomist who established experimental farms and the first agricultural teaching institute in Europe. He gave the first precise definition of humus as '… *the residue of animal and plant putrefaction*…' (cited in Feller 1997). Humus, especially the fraction soluble in boiling water, provided the 'nutritive juices' for plants (Feller *et al*. 2003).

Figure 2 - Albrecht Daniel Thaer (1752 - 1828) from La Magasin pittoresque de 1840

Thaer wrote prolifically about agriculture and is best known for his 'Principles of Rational Agriculture' published in four volumes in Berlin in the early 1800s (Feller *et al*. 2003). Although his humus theory was largely incorrect, Thaer's System of Rational Agriculture was brilliant. It was the first accounting system for soil fertility, dealing with soil-plant relationships, and it tackled the question of agricultural sustainability (Feller *et al*. 2003; Manlay *et al*. 2007). In practice though, it was a failure. The system was too complex and could not be verified since the required knowledge and analytical techniques did not exist in Thaer's day (Fussell 1971).

Thaer did leave one legacy. His promotion of humus and the interminable search for manure led progressive farmers to replace the traditional fallow with fodder crops (Fussell 1971). Productivity improved, more animals could be kept and the quantity and quality of manure increased. The use of manures, lime, chalk, marl and industrial wastes such as soap boiling ash and coal ash continued to dominate agricultural literature during the early 1800s. Pig dung was still relegated to the bottom of the heap.

The Mineralist Period [1840 – 1940]

Thaer's humus theory dominated the first half of the 19th century. However, there was a gradual shift away from the notion that humus directly fed plants. It was one of Thaer's own students who disproved humus theory. Carl Sprengel was Thaer's apprentice, then assistant, before managing large estates in Europe, studying at university and obtaining a doctorate in Natural Sciences in 1823 (Jungk 2009; van der Ploeg *et al*. 1999). Through his ongoing research work he identified 20 elements as plant nutrients and proposed the Law of the Minimum in 1828.

Sprengel's work was borrowed without proper acknowledgement by Justus von Liebig, a renowned German chemist and journal editor with over 300 scientific publications to his name (van der Ploeg *et al*. 1999). After Sprengel's death he published the Law of the Minimum as his own work. Although Liebig's work contained errors, especially in relation to nitrogen uptake (Manlay *et al*. 2007; van der Ploeg *et al*. 1999), his skill lay in his ability to collate and synthesise the available information and present it in a manner that would attract attention (Russell 1953). Liebig's book '*Organic Chemistry in its Application to Agriculture and Physiology*' was timely, controversial and drew a great deal of attention. It was translated into several languages and had many editions and reprints (van der Ploeg *et al*. 1999).

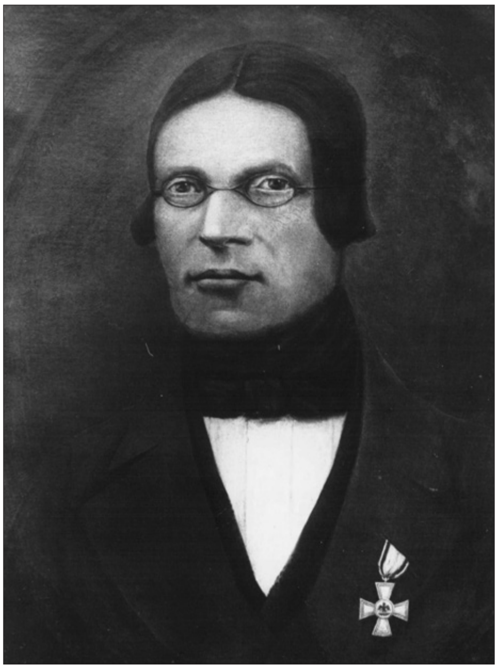


Figure 3 - Painting of Carl Sprengel (1787 - 1859)
Artist unknown

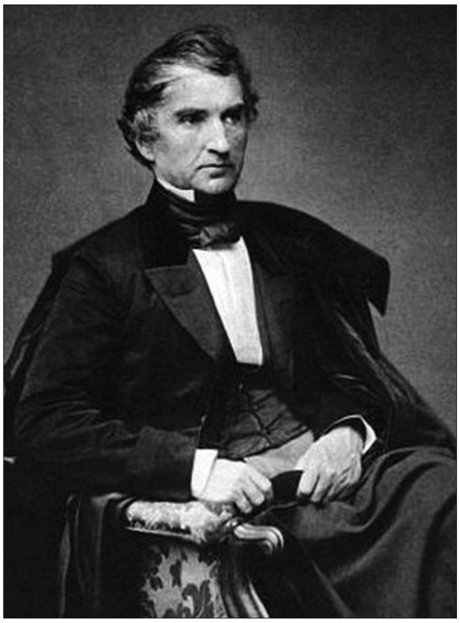


Figure 4 - Portrait of Justus von Liebig (1803 - 1873) by German artist Franz Hanfstaengl

The work came at a time when Europe's soils were exhausted from centuries of cultivation. Populations were growing in both Europe and America and farmers could not supply an increasingly urbanised society with their growing demand for food (Hyams 1976). The mineralist theory of plant nutrition began to replace the humus theory and paved the way for the establishment of the artificial fertiliser industry (Manlay *et al*. 2007).

In England, Sir John B. Lawes and Joseph H. Gilbert established the famous Rothamstead trials in 1843 (Tisdale *et al*. 1993). With other European scientists they introduced experimental method to agricultural science (Waksman 1942). Lawes and Gilbert determined that crops needed phosphorus, potassium and nitrogen, all of which could be obtained from mineral fertilisers (Tisdale *et al*. 1993).

The search for commercial sources of fertiliser was now on. Earlier in the century the English had developed a trade in tens of thousands of tons of European bones, including those from old battlefields and the catacombs of Sicily (Beaton 2010). However, bones were not a good source of phosphorus unless treated with acid, a hit and miss affair until Lawes patented the manufacture of superphosphate in 1842. Nitrates were mined in Chile and phosphates in Europe and North America. Germany opened the world's first potash factory to process potassium-rich deposits in 1857 (Beaton 2010).

In regions where the new fertiliser methods were being used, more food was grown than could be consumed (Jungk 2009). However, farmers were slow to change their ways. They had known for centuries that 'chemical manures' only stimulated plants by aiding putrefaction. Long term use might exhaust the land (Russell 1953). Humus theory was still promoted by highly regarded scientists on both sides of the Atlantic Ocean. Publications on the preparation and use of manures continued to proliferate (Fussell 1971). After all, manures provided 'fat' for the land and, though scarce, were still cheap. By 1900, artificial fertilisers only accounted for 15% of the nutrients used for cropping (Manlay *et al*. 2007).

There was another concern with the mineralist theory and subsequent exclusive use of mineral fertilisers – that it would not be sustainable (Manlay *et al*. 2007). Liebig considered nature to be a circular process with the exchange of matter between minerals, plants and animals (Marald 2002). Importing fertilisers from around the world, transporting food to the cities and washing the nutrients out to sea via water closets and rivers would lead to destruction. If mineral nutrients weren't recycled back into the soils, agriculture would become a 'robbery' system.

Liebig worked with agricultural chemists and engineers in Britain and Europe (Marald 2002). Their aim was to clean the cities of increasing loads of sewage and return it to the countryside. They looked to Asia for inspiration, especially Japan and China where human excrement had been recycled onto farms for thousands of years. Several systems were developed including barrel collection, piped sewage and pneumatic sewage removal. By 1885 more than 50 cities in Europe and Great Britain had established sewage recycling systems (Marald 2002).

Liebig's vision of recycling nutrients was short-lived. It was expensive and the entrepreneurs who were taking over sanitation by the end of the 19th century were not interested in maintaining nutrient balances between the city and the country (Marald 2002). The discovery of large fertiliser deposits and new industrial processes were improving the supply of mineral fertilisers (Beaton 2010). However, it was the discovery of microorganisms and their role in disease by Robert Koch and Louis Pasteur that sounded the death knell for recycled sewage (Manlay *et al*. 2007; Marald 2002). The new hygiene movement pronounced bacteria to be evil and physicians advocated flush toilets connected to sewerage systems that would rid homes and cities of disease causing organisms.

The Ecological Period [1940 – 2000]

Mechanisation led to the gradual intensification of agriculture during the first half of the 20th century. Fertilisers played only a minor role due largely to the economic constraints of two world wars and the Great Depression (Manlay *et al*. 2007). In America and Australia 'frontier farming' had been practised since European settlement (Henzell 2007). Land was cleared, cropped for a few seasons until depleted of sufficient nutrients and then returned to grazing with more land being cleared for cropping (Usher 1923). Land was too cheap, the areas too large and domesticated animals too few to consider manuring.

In some regions, the expansion of cropping into marginal areas led to severe soil erosion. This was starkly demonstrated in the American Mid-west where repeated ploughing and stubble burning with no crop rotation led to the infamous Dust Bowl years of the 1930s (Hyams 1976). Millions of tons of topsoil blew east to the Atlantic Ocean leaving hundreds of thousands of families destitute.

Public concerns had already been raised about the sustainability of intensive agriculture, especially where soils were continuously cropped without organic inputs (Manlay *et al***.** 2007). In response, Rudolph Steiner gave a series of lectures in 1924 to concerned farmers, from which the biodynamic farming movement developed (Merrill 1983).

Sir Albert Howard, founder of the modern organic movement, expounded his Law of Return in the 1940s (Heckman 2006). All organic waste materials should be returned via composts to the soil to build humus and fertility. Howard took a hard-line position against the use of chemical fertilisers. Organic farming was popularised in the writings of Lady Eve Balfour with her '*healthy soil, healthy plants, healthy humans*' argument (Manlay *et al*. 2007).

Figure 5 - Dust storm approaching Spearman, Texas, USA. April 14 1935. National Weather Service Weather Forecast Office Norman, OK.

In the United States Jerome Rodale spread organic and biodynamic ideas through his farming and gardening books and magazines (Heckman 2006). William Albrecht, Hans Peter Rusch and other proponents of organic farming systems continued to develop its concepts and practices. Central to their ideas was a holistic approach to agriculture, the role of humus and the return of organic matter to the soil to maintain its fertility (Manlay *et al*. 2007).

Although the notion of humus as a direct source of plant food had long been abandoned, by the 1930s researchers had developed a substantial body of information about the characteristics of humic substances, the molecules that make up humus. These included exchange, surface and colloidal properties, organo-clay complexes and the role of humic substances in soil aggregation and stability (Manlay *et al*. 2007). Several researchers had demonstrated that plants could absorb and assimilate organic compounds via their roots (Waksman 1936). Waksman (1936) identified agricultural, environmental and health benefits of humus considering it to be '… *a reserve and stabiliser for organic life… the most important source of human wealth on this planet.*'

Soil science was well established and ecology was emerging as a new discipline by the 1950s (Manlay *et al***.** 2007). Models of nutrient cycles and energy flows were being developed and the importance of detritus food webs acknowledged. After more than 100 years in the mainstream scientific wilderness, humus re-emerged under its new title 'Soil Organic Matter'.

Meanwhile, agronomists were attempting to solve the ever-present problem of feeding the world's rapidly increasing population. Fertiliser use rapidly increased in the decades following World War II (Manlay *et al*. 2007). Having experienced severe food shortages during and after the war, Europe introduced agricultural subsidies, as did the United States. Australia had introduced a superphosphate bounty during the war to offset the cost of phosphate rock (Waring and Morris 1974). Fertilisers contributed to the Green Revolution on the Indian Subcontinent and in South East Asia and Latin America (Manlay *et al*. 2007). For the first time in history whole populations, especially in the developed world, were free from hunger.

A war of words broke out between the agricultural establishment and the organic movement (Heckman 2006). To a certain extent, alternative farming systems had developed as a reaction to the reductionist approach to science and agriculture prevalent in the second half of the 20th century. At first, conventional agriculturalists simply ignored their ideas as a 'load of bunkum'. Ecological advocates complained of a perceived shift in research funding towards fertiliser-based farming (Merrill 1983).

By the 1970s the environmental movement was emerging as a social and political force. Organic gardening was growing in popularity and extending into horticulture and agriculture. Consumers began to look for residue-free produce and demand grew for a set of standards for the organic industry (Heckman 2006). Research into organic methods was being undertaken in some agricultural institutions by the 1980s. Methods once deemed too 'alternate', such as no-till and conservation farming, are now considered best practice.

By the turn of the century, and millennia, the world was reaching critical limits of agricultural land, fertile soils and potable water (Manlay *et al*. 2007). Now, agricultural scientists are becoming increasingly involved in the design of sustainable agricultural systems. A passionate debate is continuing about the relative merits of high input conventional farming versus low input alternative practices.

Manlay *et al*. (2007) have summarised the key issues:

1. Food security – Can organic farming methods reach the production levels required to feed an ever growing world population?
2. The high demand for organic inputs – Historically, there has never been enough manure and compost. Has anything changed?
3. The real costs of the two systems – How do the environmental, energy and resource costs compare? What is the true value of maintaining soil quality in agro-ecosystems?
4. Human health – What issues are caused or addressed by each system?
5. Can a rational debate progress on the basis of evidence or will it be derailed by ideology on the one hand and pragmatism on the other?

Central to this debate is the role of soil organic matter. Humus has completed the circle in its fortunes and, from relative obscurity, has returned as a central component of agricultural ecosystems and soil and plant management (Feller and Manlay 2001).

2. HUMIC SUBSTANCES

What are humic substances?

Humic substances are a mixture of exceedingly complex organic molecules that lack structural regularity (MacCarthy 2001a). At the same time they are highly chemically active yet biologically refractory, resisting microbial degradation. They are ubiquitous in nature. Sources of humic substances have been identified by a number of authors including Stevenson (1994), MacCarthy (2001a), Mayhew (2004a), Peña-Méndez *et al.* (2005) and the International Humic Substances Society (IHSS 2008).

Recalcitrant / Refractory –
Organic compounds that resist microbial degradation.

Humic substances are found in soils, sediments and natural waters such as rivers, lakes and oceans. They also represent a large proportion of the organic matter in peat bogs, carbonaceous shales, brown coals [lignites] and sewage. Humic substances contribute to the yellow and brown colours of leaf litters and composts, the dark brown or black colours of topsoil and, when in high concentrations, the brown stain in freshwater creeks and lakes. They have even been detected on the Antarctic continent (Pena-Mendez *et al.* 2005).

There is recent evidence that humic-like substances can also be found in the atmosphere (Graber and Rudich 2006). Termed 'hulis', they have been extracted from aerosol particles and water from fogs and clouds. Hulis is thought to be formed from products of combustion, terrestrial dust and aerosol particles blowing off marine spray.

Stevenson (1994) estimated that, globally, the amount of carbon held in the soil as humic substances is 6.0×10^{12} tonnes. This is from 2.0 (Piccolo 2001) to 4.5 (Simpson *et al.* 2007) times the quantity of carbon held in the living terrestrial biomass. Another major pool of organic carbon is atmospheric hulis. Muller *et al.* (2008) estimated the global dissolved organic carbon (DOC) flux in rainwater to be 430×10^6 t C/year. Depending on the region and season, hulis accounts for 15% to 60% of this airborne DOC, falling to earth in rainfall and other forms of precipitation.

Humic substances represent more than 50% (Rice 2001) and up to 80% (Pena-Mendez *et al.* 2005; Piccolo 2001) of the organic carbon in soils. Assuming an average bulk density of 1.3 g/cm^3 and an organic carbon level of 2% (Chan *et al.* 2010), Australian agricultural soils would have between 13 to 21 t/ha of humic substances in the topsoil to a depth of 10 cm.

Terminology

The terminology surrounding humic substances and fractions has historically been confusing. This situation continues today despite a call by the International Humic Substances Society (IHSS) in the 1980s for the standardisation of terms and definitions (Feller 2009).

In 1786 Achard isolated the first humic substances from soil and peat bogs using alkali solutions (Waksman 1936). During the following 140 years numerous studies were undertaken to isolate fractions of humus from different sources. Each researcher applied his own terms to and developed chemical formulae for the isolates obtained using a variety of methods. By the 1930s Waksman (1936) identified some 40 different terms for humic fractions, from humus coal through torfic and apocrenic acids to hymatomelanic acid.

Classical fractions of humus

Most of the historic terms for fractions of humus were gradually abandoned over time leaving what are considered to be the classical fractions of humus based on their solubility following treatment with an alkali (Aiken *et al.* 1985). These terms are:

> **Humic acid** – The fraction of humic substances not soluble in water at pH values lower than 2, but soluble at higher pH values.
>
> Humic acids are dark brown to black in colour (Stott and Martin 1990). They form precipitates at low pH values but become soluble as pH rises. Humic acids have long been considered as large molecules with high molecular weights. However, recent studies suggest that they might be aggregates of smaller molecules (Pena-Mendez *et al*. 2005).
>
> **Fulvic acid** – The fraction of humic substances soluble in water under all pH conditions.
>
> Fulvic acids change colour depending on pH (Stevenson 1994). At very low pH values they are a straw yellow colour. As pH rises to 3 they turn orange and then wine red at higher pH readings. Fulvic acids are generally considered to be smaller molecules with lower molecular weights than humic acids. However, there is no agreed standard on the distinction between humic and fulvic acids based on molecular weight (Mayhew 2004b).
>
> **Humin** – The fraction of humic substances not soluble in water at any pH value.
>
> Very little is known about humin. It is the oldest of the three fractions and is at the point in the carbon cycle where plant remains are turning into unlithified sediments (Rice 2001). Although humin accounts for more than 50% of the organic carbon in soils, few studies have been conducted with this material due to its insolubility under classical extraction methods (Song *et al*. 2008). Stevenson (1994) suggested that it may be inappropriate to designate humin as a separate fraction. In the early 1990s it was thought that the insolubility of humin may be due to a very close association with mineral matter in the soil and that it might simply be an artefact of the fractionation process. More recent studies have shown that humin treated with a comprehensive extraction procedure was composed of plant and microbial derived components in a fine clay matrix (Song *et al*. 2008).

The value of all three terms, humic acid, fulvic acid and humin, is being increasingly questioned as improved analytical techniques shed new light on humic substances. Separation on the basis of solubility creates an operational distinction but does not indicate whether the three are different types of organic molecules (Sutton and Sposito 2005) even though they are commonly thought to be. Feller (1997) suggested that the extracted fractions may simply be the result of chemical denaturation of the original humic compounds and may not actually exist in soil.

The terms 'humic acid' and 'fulvic acid' are in themselves somewhat of a misnomer. 'Humic acid' was coined in the early 1800s when chemistry and especially organic chemistry were new disciplines (Waksman 1936). Fulvic acid replaced a raft of names for the soluble fraction of humus, such as apoglucic acid and porla-crenic acid. Definitions were fluid and the rules of nomenclature, which would be established during the 20th century, did not yet exist.

Humic acid, a precipitate produced by adding acid to an alkali solution, is a salt and could more correctly be called 'humate' (Mayhew 2004a). Humic and fulvic acids do exhibit the properties of weak-acid polyelectrolytes, large molecules with the ability to donate numbers of hydrogen ions into solution. They provide a buffering capacity over a wide range of pH values (Stevenson 1994). However, this is only one of a number of functions that characterise humic substances.

Polyelectrolyte -

A large molecule (polymer) with repeating structural units that each carry an electrolyte group. These groups dissociate in water leaving a net electric charge on the polymer.

Humus and soil organic matter

As humus assumed its more modern name, soil organic matter (SOM), and analytical techniques improved, a number of fractions were identified and attempts made to separate humic substances from other SOM. Table 1 summarises the evolution of the relationship between humic substances and SOM.

Stevenson (1994) divided SOM into litter, the light fraction, microbial biomass, water soluble organics, soil enzymes and passive humus. He also divided SOM into two pools: the active, or labile pool; and the stable, humus pool. The active pool provided a ready source of nutrients for plant growth, depending on the rate of microbial decomposition. The stable pool provided a reservoir of nutrients and was important for long-term soil balance. More recently, some authors (von Lützow *et al*. 2008; Wander 2004) have included an intermediate or slow pool, in which they have placed mobile humic substances.

Table 1 - The evolution of the relationship between humic substances and SOM

	Humic substances	and SOM		
McCarthy *et al*. (1990)	Litter Light fraction	Microbes Enzymes	Water soluble organics (Non-humic)	Humus (Humic)
Stevenson (1994)	Litter Light fraction	Microbes Enzymes	Water soluble organics	Humus
Sutton and Sposito (2005)	Litter Light fraction	Microbes Enzymes	Water soluble organics	Humus

MacCarthy *et al*. (1990b) had suggested a more narrow definition of SOM than Stevenson. It was the organic part of soil excluding the undecayed material, that is, the litter and a proportion of the light fraction. They then divided SOM into humic and non-humic fractions. Non-humic substances were discrete organic compounds that could be purified and had a definite molecular structure. They included polysaccharides, sugars, proteins and amino acids. Humic substances were, basically, everything else – the non-specific organic material for which a definite structure had not yet been determined.

Decades of research have been devoted to the quest to separate humic and non-humic substances and solve the humic conundrum. However, recent advances in analytical techniques have shed new light on the role of ″non-humic″ materials within humic substances. Having conducted a critical examination of published data, Sutton and Sposito (2005) found that recognisable biomolecular fragments, such as carbohydrates, proteins, lipids and lignins, were strongly associated with humic fractions. They could find no reason to exclude these biomolecules from definitions of humic substances as had traditionally been done.

Definitions of the term 'humic substances' itself have evolved through recent decades with the improvement in analytical techniques and subsequent development of new structural models. The most commonly quoted definitions/descriptions can be found in Appendix 1. Recently, the terms humic substances and humus have gradually been replaced in the literature with NOM (non-living natural organic matter). NOM variously includes: soil and dissolved humic substances (Wershaw and Goljer 2001); humic substances and other recalcitrant materials, such as tannins and lignins (Keiluweit and Kleber 2009); and humic and non-humic substances (Diallo *et al.* 2001).

Characteristics of humic substances

It is now widely recognised that humic substances provide the structural and functional properties in soil that have been more broadly attributed to SOM. These characteristics have been well documented in a significant body of literature including texts edited and/or authored by: MacCarthy *et al*. (1990a); Stevenson (1994); Davies and Ghabbour (1998); Ghabbour and Davies (2000); Ghabbour and Davies (2001); Magdoff and Weil (2004); and Perminova *et al*. (2005).

The functions of humic substances, which will be described in more detail in Section 4, include:

» **Physical characteristics** – Formation of organo-clay complexes and resulting stable aggregates; improvement of water holding capacity; and soil temperature regulation.

» **Chemical characteristics** – Formation of colloids; source and sink of plant nutrients; electrochemical and ion exchange properties; amphiphilic properties and aggregation into membranes and micelles; complexation with metal ions and chelation reactions; and adsorption of organic chemicals including pesticides.

» **Biological characteristics** – Energy and nutrient source for micro-organisms; control of plant pathogens; and hormone-like activity in plant growth.

It is the two somewhat contradictory characteristics of humic substances that enable them to play such diverse roles in soil. They are extremely reactive with a large number of chemically active functional groups contained within their structure (Stevenson 1994). At the same time they are highly refractory or recalcitrant. That is, humic substances resist decomposition by soil microorganisms and enzymes. Other organic compounds could carry out the functions of humic substances but they simply don't survive long enough in soil before they are decomposed.

> *Humic substances constitute the only natural organic material that can survive in bulk and still possess the requisite chemical reactivity to perform the various functions for sustaining soil quality and promoting plant growth (MacCarthy 2001a).*

How humic substances achieve this is determined by their formation and structure. Scientists have spent more than 200 years attempting to solve this puzzle. Although not yet resolved, advances in the last decade have shed considerable light on the topic.

Formation and structure of humic substances

Humification is the term used to describe the chemical and microbiological processes that transform the dead remains of living things into humic substances. It is the second greatest process on earth after photosynthesis involving from 20 (Perminova *et al*. 2005) to 75 (Marschner *et al*. 2008) gigatonnes of carbon each year. Himes (1998) estimated that the sequestration of 10 tonnes of carbon into humus requires 28 tonnes of C or 62 tonnes of dry organic residue. In addition, 833 kg of nitrogen, 200 kg of phosphorus and 143 kg of sulphur are bound into the humic molecules. This gives a C/N/P/S ratio of 120:10:2.4:1.7. However, as these nutrients are held tightly in the humic structure, their availability to plants is relatively low (Stevenson 1994).

The genesis of humic substances can take hundreds or even thousands of years (Balser 2005) making direct observation impracticable, if not impossible. To study them, researchers have extracted humic substances from soil and other sources and used a range of chemical and physical analytical methods that have become more sophisticated over time. Fathoming the formation and structure of humic substances has become a scientific chicken and egg scenario. Understanding their genesis will reveal their structure, but knowledge of the structure is needed to determine the pathways of formation. Despite decades of research the subject is still not settled.

The structure of humic substances

Understanding the structure of humic substances is essential for the explanation of their many functions (Stevenson 1994) and has considerable implications for soil, agricultural and environmental management (Hayes and Clapp 2001). The empirical formula, the ratio of atoms present in a sample of humic material, is determined from the elemental composition of the sample. Tables 2 and 3 show the mean elemental composition and range for humic and fulvic acids respectively, compiled from the literature for a variety of source materials. A list of the references used can be found in Appendix 2. The wide range of results is a reflection of the variation in materials from the same type of source and the use of different extraction methods and analytical techniques.

Table 2 - Mean elemental composition of humic acids extracted from a variety of sources

Source material (% weight*)	C	O	H	N	S	P	Ash
Soils**	55.3 (37.2 – 64.1) *n = 235*	36.0 (27.1 – 52.0) *n = 227*	4.8 (1.6 – 8.0) *n = 235*	3.6 (0.5 – 7.0) *n = 235*	0.8 (0.1 – 4.9) *n = 227*	0.6 (0.1 – 1.0) *n = 2*	1.1 (0.2 – 2.1) *n = 11*
Peats	57.1 (49.9 – 62.8) *n = 26*	35.7 (30.7 – 43.6) *n = 26*	5.0 (3.6 – 6.6) *n = 26*	2.7 (0.6 – 3.9) *n = 24*	0.6 (0.1 – 2.4) *n =14*	No data available	16.0 (1.1 – 31.0) *n = 2*
Brown coals	52.9 (32.0 – 65.2) *n = 25*	33.6 (26.8 – 48.5) *n = 8*	4.4 (3.0 – 11.0) *n = 15*	1.6 (1.0 – 2.9) *n = 15*	1.4 (0.4 – 3.3) *n = 17*	No data available	14.0 (1.0 – 42.0) *n = 18*
Commercial products	61.9 (52.9 – 69.0) *n = 28*	35.0 (25.1 – 43.5) *n = 27*	5.3 (3.6 – 6.8) *n = 28*	0.8 (0.3 – 2.1) *n = 8*	2.9 (0.4 – 4.6) *n = 20*	0.1 (0.0 – 0.2) *n = 17*	18.5 (2.7 – 32.8) *n = 26*
Organic materials	50 (35.3 – 57.3) *n = 8*	38.2 (36.8 – 39.6) *n = 2*	5.3 (3.6 – 8.1) *n = 7*	3.9 (0.9 – 7.5) *n = 8*	No data available	No data available	1.3 (0.7 – 1.9) *n = 5*

(Range); *n = number of samples*

Table 3 - Mean elemental composition of fulvic acids extracted from a variety of sources

Source material (% weight*)	C	O	H	N	S	P	Ash
Soils**	33.8 (35.1 – 75.4) *n = 179*	46.1 (16.9 – 55.9) *n = 131*	5.0 (3.0 – 7.0) *n = 133*	2.6 (0.5 – 5.9) *n = 133*	1.2 (0.1 – 3.6) *n = 50*	0.3 (0.1 – 0.6) *n = 2*	2.8 (0.6 – 10.5) *n = 6*
Peats	54.2 (46.9 – 60.8) *n = 12*	37.8 (31.1 – 44.3) *n = 12*	5.3 (4.2 – 7.2) *n = 12*	2.0 (1.2 – 2.6) *n = 1*	0.8 (0.2 – 1.9) *n =12*	No data available	No data available
Brown coals	43.8 (38.0 – 46.9) *n = 4*	No data available	4.3 (4.0 – 4.7) *n = 4*	4.0 (1.5 – 9.9) *n = 4*	No data available	No data available	1.9 (1.5 – 2.6) *n = 4*
Commercial products	48.9 *n = 1*	No data available	4.0 *n = 1*	0.5 *n = 1*	No data available	No data available	1.0 *n = 1*
Organic materials	48.5 (48.1 – 48.9) *n = 2*	No data available	4.4 (4.1 – 4.7) *n = 2*	0.6 (0.5 – 0.7) *n = 2*	No data available	No data available	1.3 (1.0 – 1.5) *n = 2*

(Range); *n = number of samples*

* Note – Most results for elemental composition included in the above tables were reported on an ash and moisture free (oven dry) basis. Some papers, however, recorded the units only as percentage weight or equivalent unit with no basis provided for the calculation. This highlights a major problem when dealing with humic materials. Even in the scientific literature there is no standard protocol for reporting results. To add to the confusion, a wide range of extraction methods was used to isolate the humic and fulvic acids from their source materials.
** Note – The large sample number for elemental composition of soil humic and fulvic acids results from an extensive review of the literature conducted by Rice and MacCarthy (1991) to which more recent analyses have been added.

Structural models of humic substances

Several structural models have been proposed for humic substances with accompanying theories for their formation. These models can be broadly divided into two main schools of thought, the macromolecule and the supramolecular mixture.

Macromolecule -

A very large molecule usually formed by the process of polymerisation where smaller molecules combine chemically to form three-dimensional networks or polymer chains.

Supramolecular mixture -

Smaller molecules held together in a larger assembly by noncovalent interactions such as hydrogen bonding, hydrophobic forces and van der Waal's forces.

Macromolecular theory

The first school of thought is a series of models that consider humic substances to be extremely large macromolecules with molecular weights of several hundred thousand (Stevenson 1994) to over a million daltons (Hayes and Clapp 2001; Simpson 2002). To put this in perspective, one glucose molecule has a molecular weight of 180 Da.

The macromolecular models have been developed from the results of traditional analytical methods involving the physical or chemical degradation of larger humic molecules into smaller pieces (Balser 2005). The resulting subunits are isolated, identified and measured then put back together again into structural models. It's like doing a large, complicated three-dimensional jigsaw puzzle without the pictures. Balser (2005) used the analogy of smashing a watch with a sledge hammer and asking someone to both reconstruct the watch and explain how it was originally made. The additional challenge of humic substances is that no one knows what they looked like in the first place.

According to the models, the macromolecules have an aromatic backbone (Stevenson 1994). Aromatic molecules are based on the benzene ring. The arrangement and sharing of electrons around the ring make benzene and its derivatives particularly stable molecules. This aromaticity contributes to the refractory nature of humic substances. Aliphatic [non-aromatic] structures are attached to the chains of aromatic rings (Figure 6), as are numerous oxygen and nitrogen functional groups (Stevenson 1994). The main difference between these models is the source of carbon and the pathways of microbial transformation. Lignins, sugars, amino compounds, polyphenols and quinones have all been suggested as precursors to humic substances.

In organic chemistry, aliphatic and aromatic are opposites, that is, an aliphatic compound can also be called a non-aromatic compound.

Aromatic -

An organic compound based on the benzene ring. Aromatic molecules are more chemically stable than similar non-aromatic molecules because the electrons are shared between all the carbon atoms in the ring.

Aliphatic -

Organic compounds with the carbon atoms arranged in straight or branched chains, or non-aromatic saturated rings, where all the available bonds to the carbon atoms are occupied.

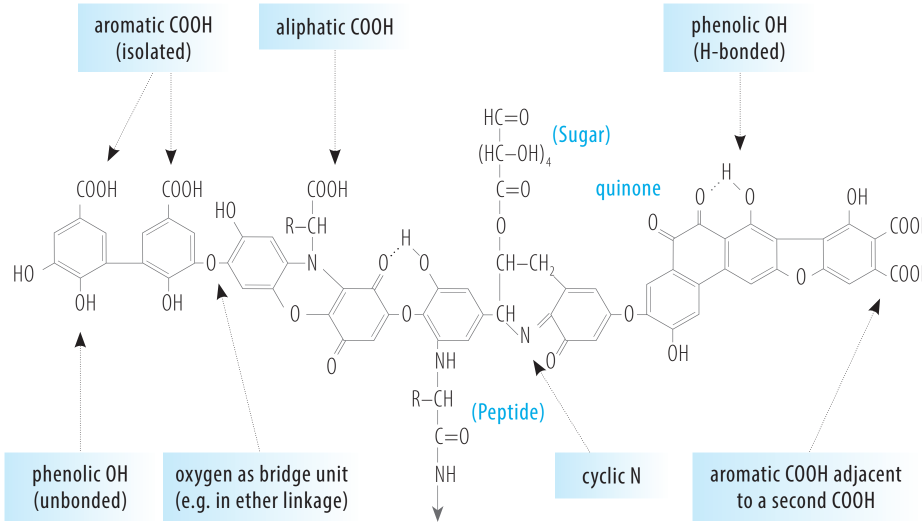


Figure 6 - Hypothetical structure of a humic acid showing an aromatic backbone, aliphatic side chains and oxygen and nitrogen functional groups. From Stevenson, *Humus Chemistry - Genesis, Composition, Reactions*, 2nd Edition. Copyright © 1994 by John Wiley & Sons, adapted with permission of John Wiley & Sons, Inc.

By the turn of this century a number of researchers were seriously questioning the macromolecular theories of humic substances. In the light of new data from improved analytical techniques, especially physical fractionation and pyrolysis, they found little evidence to support the traditional models (Burdon 2001; Hayes and Clapp 2001; MacCarthy 2001a; Piccolo 2001; Sutton and Sposito 2005). New non-degradative techniques are now being used to unravel the structure of humic substances (Balser 2005). They include: solid-state nuclear magnetic resonance (NMR); ultraviolet-visible and infrared spectrometry; electron spin resonance (ESR) spectrometry; X-ray analysis; electron microscopy; and electron diffraction. These methods keep the humic molecules intact, avoiding the artefacts of traditional degradative analysis, and indicate different structures for humic substances (Balser 2005).

Supramolecular theory

A new theory was developed which MacCarthy (2001a) summarised in his First and Second Principles of Humic Substances together with a series of corollaries. According to the new view, humic substances are a mixture of diverse but much smaller molecules with molecular weights less than 2000 Da (Simpson *et al.* 2002). These largely aliphatic molecules (Simpson *et al.* 2002) combine in a random fashion forming dynamic associations that are held together by hydrogen bonds and hydrophobic interactions (Sutton and Sposito 2005). Recently, Huang and Hardie (2009) suggested that, since there is no conclusive evidence to disprove either the macromolecular or the supramolecular theories, humic substances may have the characteristics of both.

Hydrogen bonds –

Hydrogen atoms attached to a molecule can develop a net positive charge attracting them to electronegative atoms such as nitrogen, oxygen and chlorine. They form relatively strong bonds between different molecules or different chemical groups on the same molecule.

Hydrophobic bonds/forces/ interactions –

Molecules that have no net electric charge are non-polar and hydrophobic, or water-fearing. As they repel water, the individual hydrophobic molecules tend to clump together.

The reactivity of humic substances

Regardless of their ultimate structure, humic substances are highly chemically reactive due to the large number of functional groups attached to the humic molecules (MacCarthy 2001b). Figure 6 shows a hypothetical structure of humic acid with several oxygen and nitrogen functional groups attached. Foremost amongst these are the carboxyl and phenolic groups. These oxygen functional groups are acidic, donating protons (H^+ ions) into solution and contributing to the ion-exchange properties and complexation reactions of humic molecules (Figure 7). Carboxyl and phenolic groups are abundant in humic materials with other weakly acidic alcohol-OH groups also contributing to the chemical reactivity.

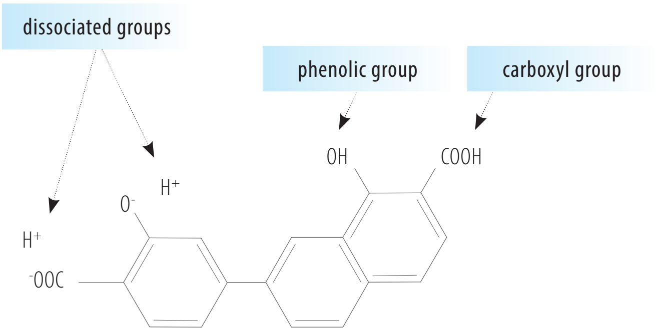


Figure 7 - Portion of a hypothetical humic molecule with carboxyl and phenolic groups in their undissociated and dissociated forms.

The chemical reactivity of a particular humic material is often measured as total acidity. It can refer to the carboxylic and phenolic-OH groups only or to all of the oxygen functional groups (Stevenson 1994). As with elemental composition, there is a wide range of results for samples from the same type of source and different analytical methods can give different results for the same sample. Table 4 shows the total acidities for a range of humic materials compiled from the literature. In general, fulvic acids have a higher total acidity than humic acids (Pena-Mendez *et al*. 2005) largely due to a higher content of COOH groups (Stevenson 1994). Given their higher total acidity and smaller molecular size, fulvic acids are often considered to be more chemically and biologically active than humic acids though this is yet to be established (Mayhew 2004b).

The formation of humic substances

There are as many theories for the formation of humic substances as there are structural models. Stevenson (1994) has summarised these theories as have, more recently, Hayes (2009) and Huang and Hardie (2009). In general, the formation of stable humic substances depends on the selective preservation of recalcitrant organic molecules, that is, their ability to resist initial microbial decomposition, and the synthesis of even more recalcitrant molecules (Huang and Hardie 2009).

The factors that affect the genesis of humic substances are similar to those proposed by Jenny for soil formation (Stevenson 1994). They include climate, soil factors, vegetation and time (Chan *et al*. 2010). Microorganisms are intimately involved in the humification process (Balser 2005), both in the decomposition of organic residues and the synthesis of humic molecules. Therefore, a soil environment that promotes microbial activity will lead to carbon storage in the form of humus. Water and oxygen availability, pH, temperature and soil type all play a role as does the quality and quantity of plant litter and the composition and activity of the microbial community.

Table 4 - Acidic functional group analysis of humic and fulvic acids extracted from the source material.

Source material (meq/g)	COOH	Phenolic-OH	Total acidity
Humic acids			
Soils	3.3 (0.7 – 6.2) *n = 13*	1.9 (0.1 – 5.7) *n = 13*	5.6 (1.4 – 8.9) *n = 21*
Peats	2.7 (1.3 – 4.4) *n = 6*	1.4 (0.3 – 3.8) *n = 6*	4.4 (2.0 – 8.2) *n = 6*
Brown coals	3.7 (2.0 – 7.0) *n = 15*	3.0 (0.9 – 5.6) *n = 15*	6.7 (4.9 – 9.8) *n = 15*
Commercial products	2.6 (0.5 – 5.8) n = 8	2.2 (1.9 – 2.8) n = 8	4.9 (2.4 – 8.6) n = 10
Organic materials	4.5 (3.1 – 5.3) *n = 3*	3.2 (2.5 – 4.3) *n = 3*	7.7 (7.5 – 8.1) *n = 3*
Fulvic acids			
Soils	6.8 (5.2 – 11.2) *n = 6*	3.1 (0.3 – 6.7) *n = 6*	9.7 (6.4 – 14.2) *n = 6*
Peats	No data available	No data available	No data available
Brown coals	6.6 *n = 1*	5.0 *n = 1*	11.6 *n = 6*
Commercial products	8.3 *n = 1*	0.9 *n = 1*	9.2 *n = 1*
Organic materials	8.2 (8.0 – 8.3) *n = 2*	1.1 (0.9 – 1.4) *n = 2*	9.3 (9.2 – 9.4) *n = 2*

(Range); *n = number of samples*
Note – A list of the references used in this table can be found in Appendix 2.

The initial phase of humification involves the physical breakdown, redistribution and enzymatic alteration of plant litter by soil fauna (Huang and Hardie 2009). This is followed by the rapid decomposition of the labile fraction. Soluble, low molecular weight compounds, such as sugars, proteins and organic acids, are preferentially ingested by microorganisms. They provide a carbon and nitrogen source for energy, growth and reproduction of the biomass often with the accompanying assimilation and immobilisation of nutrients from the soil (Balser 2005).

As the available carbon sources are used up, there is an accumulation of more recalcitrant molecules. Cellulose, hemicellulose, lignin, lipids, tannins and waxes such as cutin and suberin make up the structural components of plant cells and are all too large to be directly ingested by microorganisms (Balser 2005). Saprophytic bacteria and fungi produce extracellular enzymes that break these larger compounds into smaller molecules that can then be assimilated. Fungi, especially the white rot and brown rot species, are the most efficient decomposers of cellulose and lignin (Huang and Hardie 2009). Microorganisms capable of degrading organic residues, including lignin, are found in virtually all soils. They vary only in numbers and proportions. If this were not so, the world would be buried in plant residues and there would be no carbon dioxide left in the atmosphere (Stevenson 1994).

During the process of decomposition and assimilation, microorganisms produce a number of recalcitrant compounds of their own. They include chitins, melanins, lipoproteins and phospholipids (Huang and Hardie 2009). These molecules become part of the substrate mix available for the synthesis of humic substances when the microorganisms die and are, themselves, broken down. Studies of undisturbed soil profiles, for example forest floors, show a gradation from plant-derived humus nearer the surface to that of microbial origin with increasing depth (Balser 2005). The use of marker compounds has shown that microbial products accumulate in humic substances as a function of age as well as soil depth.

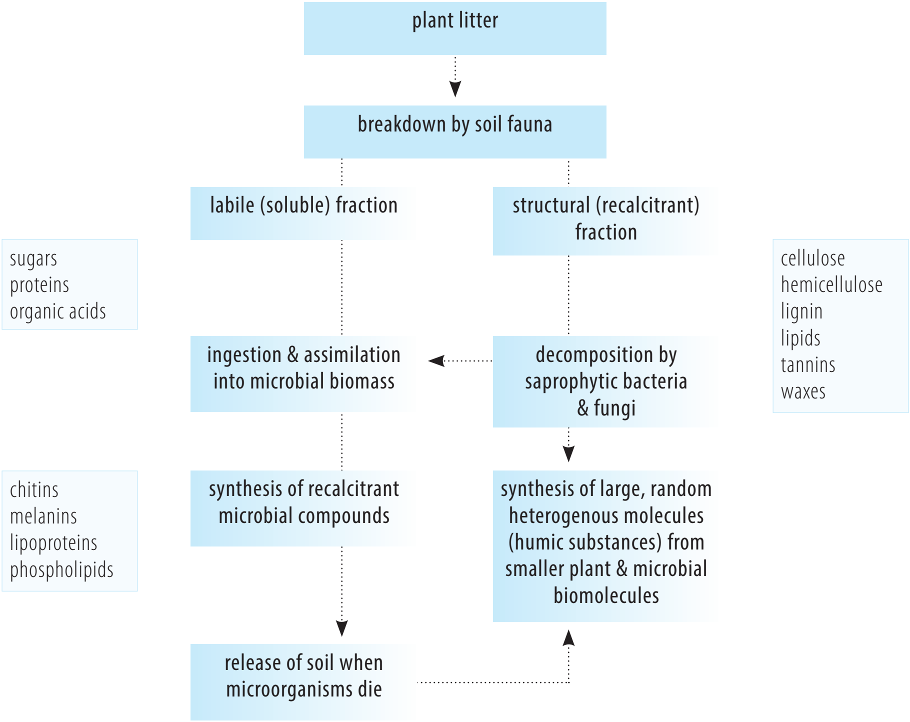


Figure 8 - The process of humification

The final phase in humification is the synthesis of larger, random, heterogeneous molecules from the smaller, decomposed, structurally-organised biomolecules of plant and microbial origin (Huang and Hardie 2009). For example, the long chain of a partially degraded lignin or tannin molecule may serve as the aromatic 'backbone' of a humic molecule to which is added several chains of single-bonded carbons [alkyls] from plant cuticles (Balser 2005). Both extracellular enzymes, produced by microorganisms, and soil minerals act as catalysts for these synthesis processes. Their relative importance depends on the source of vegetation, microbial activity and the mineralogical composition of the soil (Huang and Hardie 2009). The various formation theories differ in terms of the substrates and chemical pathways involved in the synthesis mechanisms. It could be that all the known formation reactions contribute to the genesis of humic substances (Stevenson 1994).

Long-term stabilisation of humic substances

It is the sheer randomness of their formation and the resulting molecular heterogeneity that cause humic substances to be refractory (MacCarthy 2001a). If each humic macromolecule or supermixture is unique, the number of microorganisms and specialised enzymes needed to dismantle the structure would be enormous. It is not that humic substances are never broken down by microorganisms; they just need a long time to do it.

The extracellular enzymes produced by microorganisms to decompose organic matter are designed to bind to and break down regular repeating carbon units (Balser 2005). If a microbial enzyme meets that same carbon unit in the irregular humic matrix, it will undo the bonds. This degradation of humic molecules occurs incidentally to the original purpose of the enzymes in a process called 'cometabolism'. Some extracellular enzymes become stabilised on mineral surfaces where they can remain active for years. They are also responsible for the 'accidental' breaking down of humic molecules, contributing to their turnover in soils.

As humic substances avoid microbial degradation they become increasingly inert resulting in long-term stability (Kastner and Hofrichter 2001). This, however, requires more than their resistance to decomposition. According to research first conducted by Wershaw (1986) and confirmed by others (Piccolo 2001; Sutton and Sposito 2005), humic substances are amphiphiles and form micelle or membrane-like aggregates with hydrophobic [water-fearing] interiors and hydrophilic (water-loving) exteriors (Figure 9). The highly charged hydrophilic surfaces interact with minerals in the soil while the hydrophobic centres repel water and reduce access for microbial enzymes (von Lützow *et al*. 2008).

Cometabolism –

The degradation of two compounds by the same microbial enzyme. The first compound serves as an energy source while the second compound, which is not used for growth by microorganisms, is also transformed.

Hydrophilic – (Water-loving)

A molecule or part of a molecule that is attracted to water due to its net electric charge.

Hydrophobic – (Water-fearing)

A molecule or part of a molecule that has no net electric charge and therefore repels water.

Amphiphile –

A molecule with both hydrophilic and hydrophobic parts. The hydrophilic end of the molecule is attracted to water and the other, non-polar end is attracted to solvents such as oils.

Micelle –

An aggregate or cluster of molecules suspended in water. The molecules often align so that their hydrophobic tails are buried in the centre of the micelle with the hydrophilic heads facing out and adsorbing onto the surrounding water molecules.

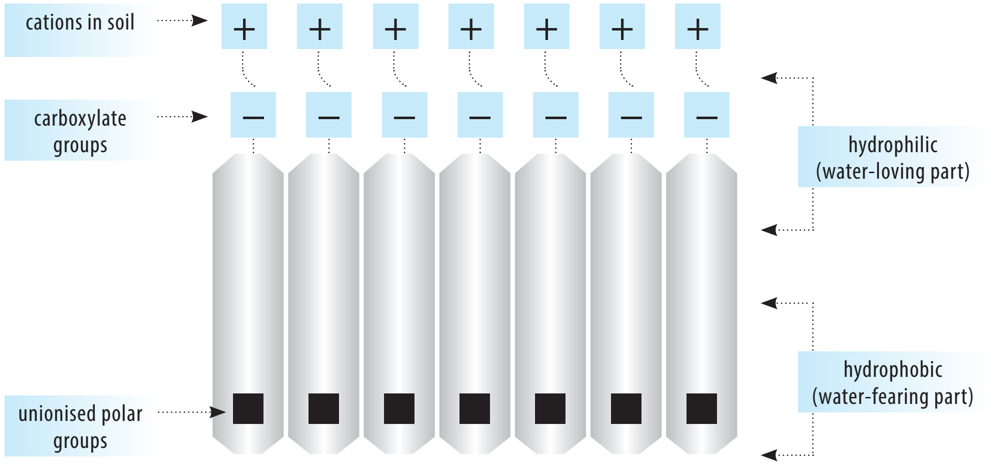


Figure 9 - Membrane-like humic aggregate showing its amphiphilic nature with a hydrophobic part at the non-polar end and a highly charged hydrophilic part at the polar end

Soil type has a major impact on the physical protection of humic substances. Those soils with a higher proportion of silt and clay store more carbon than sandy soils (Balser 2005). Soil mineral colloids, especially aluminium and iron oxyhydroxides, complex with humic substances and protect them from enzymes (Huang and Hardie 2009). Soil structure is also involved. Soils with good aggregate structure store more carbon than those with poor structure. Humic molecules formed in clay micropores are protected due to the spatial inaccessibility for microbes (von Lützow *et al*. 2008).

Black carbon may also play an important role in the formation and long-term stabilisation of humic substances. It is the finer fraction of pyrogenic carbon, that is, soot and char which resists chemical oxidation (Huang and Hardie 2009). Song (2008) extracted black carbon from a Mollisol soil used as a standard by the International Humic Substances Society. Laird *et al***.** (2008) found significant amounts of pyrogenic black carbon and charcoal in both prairie and agricultural soils in the USA. They and Keiluweit and Kleber (2009) have suggested that it is the black carbon in soils that is responsible for the recalcitrance of humic substances. Huang and Hardie (2009) noted the importance of black carbon in volcanic regions and where there are frequent fires or annual stubble burning is practised.

The age of humic substances

Due to the gradual turnover of humic substances in soils it is not possible to follow and date an individual molecule. Torn *et al*. (2009) reviewed the storage and turnover of organic matter in soils. The age of organic matter, including humic substances, in a particular soil can be measured and expressed using the following terms:

- **Turnover time** – the time taken to completely empty the reservoir if there are no new inputs.
- **Mean (average) residence time** – The average time an individual carbon atom has spent in the reservoir at the point when it leaves.
- **Average age** – The average time that all of the carbon atoms currently in the reservoir will spend there.

Carbon isotope tracing with ^{13}C and ^{14}C atoms are used in these measurements. Stevenson (1994) reviewed the mean residence times of humus from soils in Canada and the United States. They ranged from 250 to 3280 years. In their review, Kastner and Hofricter (2001) noted that natural humic substances ranged in average age from a few months to several thousands of years.

3. HUMIC PRODUCTS

What are humic products?

Humic products were first produced in the early 1800s (Waksman 1936). Termed 'artificial ulmins', they were made by treating starches and sugars with sulphuric or hydrochloric acid. The dark liquid that was obtained precipitated to a black substance similar to the humic acids that were being isolated from peats, soils and rotting plant materials.

Almost 150 years later, Burdick (1965) commented that, although very pure humic acids and humate concentrates had long been laboratory curiosities, they had not been developed commercially as fertilisers for agriculture. This was despite the fact that the beneficial properties of humic substances in soils were well established and trials had indicated the role of purified humates in germination, root growth and crop yield. Synthetic polymers had been developed and marketed with some success but their high cost and rapid loss of effectiveness limited their use.

Burdick (1965) suggested that, even though an economical and practical manufacturing process was available, it was the lack of suitable raw materials that was preventing the expansion of the commercial humic market. At that time deposits of brown coals and 'aguja', an organic mineral soil found in Texas, were being surveyed and their properties analysed.

By the 1980s, the emerging alternative fertiliser industry was beginning to manufacture and market commercial humic products. Many were sourced from brown coals or lignites, soft friable coals with a dull earthy appearance and low carbon and, therefore, low energy content relative to hard coals (ACA 2008). Prized among the brown coals was, and still is, leonardite. Leonardites contain up to 85% humic acid but less than 7% fulvic acid on laboratory fractionation analysis (Dailey 1999). In Australia, the brown coal deposits of Victoria's La Trobe Valley provide lignite and leonardite for the commercial humate market which has burgeoned since the early 1990s. Products are also sourced from peats, lignins and composts.

Most humic products are prepared by alkali extraction of brown coals with sodium, potassium and ammonium hydroxides and the resulting salts are termed humates (Perminova and Hatfield 2005). Some companies also sell natural, organic or "raw" humates which have not undergone alkali extraction. According to the USA Organic Materials Review Institute (OMRI 2010), alkali extracted humic acids are allowed in organic certification schemes as long as the amount of synthetic alkali [e.g. potassium hydroxide] does not exceed that required for extraction and does not fortify the product with nutrients. Similarly, fulvic acids extracted by the use of hydrolysis or naturally occurring acids can also be used.

Figure 10 – A commercial granular humic product

To a large extent humic products are considered to be an amendment to, not a replacement for, regular fertilisers. Manufacturers make the broad claim that, given an existing or even reduced fertiliser regime, the use of their product will increase fertiliser efficiency and plant growth and improve soil quality and plant health. These products were originally used in broadcast and foliar applications. The liquid form of the foliar sprays was easier to use than the dusty dry materials but the low application rates had no effect on soils (Mayhew 2004a). The products were only compatible with high-pH liquids or precipitation would occur. A pelletised form of leonardite was developed by the US Bureau of Mines, University of Dakota (Mayhew 2004a). It enabled the humic products to be combined with various ratios of standard NPK fertilisers. Foliar and fertigation products are now available that are soluble in water.

The proliferation of humic products being sold under a variety of names has added to the confusion in terminology already surrounding humic substances. Mayhew (2004a) identified more than 20 different names used to describe commercial humic products. These include: the classical names, humic and fulvic acids and humin; less common names such as slack lignite, humalite and humic shale; and the archaic term 'ulmic acid'. In the USA, more than 70 different products are registered with the Organic Materials Review Institute (OMRI 2010). There are many more that are not listed with this organisation. The use of trade names without listing the contents using agreed terminology, such as occurs with conventional fertilisers and medicines, is a major concern with these products.

The situation is not much different in Australia. An extensive web search conducted by the author in February 2012 uncovered 28 different Australian companies selling more than 200 humic products with a wide use of terms and trade names.

Survey of Australian companies selling humic products

The information from the websites of 15 Australian companies, chosen for their promotion of humic products for broadacre cropping and pasture production, has been collated and summarised. The survey was conducted in February 2012. Given that the companies are advocating the importance of humic substances for soil health and plant growth, the information has been analysed in the light of current scientific information about humic substances.

Company and product names are not given in this review but the list of companies and web addresses can be found in Appendix 3. This survey reflects the information solely available to the public via the company websites at the time of writing.

General information

- Six companies were based in Victoria, two in New South Wales and three each in Queensland and South Australia. One company had offices in all six Australian states.
- The number of products per company ranged from one to three all-purpose types to more than 70 different blends with plant macro and micronutrients.
- Four companies sourced products from other Australian and overseas manufacturers. The other eleven companies manufactured their own products.
- Four of the manufacturers used brown coals or natural black peats with two specifying leonardite extracted from Victorian brown coals. Two manufacturers used organic matter, such as lignin or kelp. Five companies provided no information about their product sources.
- Concentrations of active humic or fulvic ingredients ranged from 0.16% to 26% for liquid products and 5% to 85% for solid products.
- All but three companies provided accessible information about application rates. One of these had the information scattered throughout a large body of text. Another would provide application rates following contact with the company. There was a huge variation in rates amongst the twelve companies that posted this information on their websites:
  - Humate-nutrient granules ranged from 10 – 400 kg/ha broadcast and 5 – 100 kg/ha side dressed.
  - Natural, organic or 'raw' humates were to be banded from 200 – 500 kg/ha and broadcast from 200 kg to 1 tonne/ha.
  - One company had very low application rates from 37 – 438 ml/ha added to liquid nutrient and other solutions.
  - Most liquid or foliar sprays ranged from 1 – 50 L/ha depending on the product and application. For example, one company's recommendation for sodium management was 1 – 2 L/ha and for soil detoxification, 50 L/ha. Where dilution rates were given they ranged from 1:10 to 1:200.

- Only six companies provided information about the timing and frequency of product applications. These varied depending on the type of crop and stage of growth. Foliar applications were as frequent as every 10 to 14 days. One website recommended pasture applications every four to six weeks whereas another advised two to four applications to pasture during the growing season. One company did not provide information on their website but suggested that farmers should consult with the distributor about application rates and timing.
- None of the manufacturers provided prices on their websites. Two distributors had granular products listed from \$65.00/25 kg (\$2.60/kg or \$2,600/t) to \$39.00/5 kg (\$7.80/kg or \$7,800/t). Liquid products were listed at \$35 for a 5 kg drum (\$7/kg) and \$75.90 for 4 litres (\$18.96/L). A third distributor had one liquid product listed at \$170.50 per 20 L drum (\$8.53/L) and another at \$1905.75 for a 200 L drum (\$9.53/L).
- Five companies had registered their products with the Biological Farmers of Australia (BFA) organisation. One company was registered with the National Association for Sustainable Agriculture, Australia (NASAA) and another with both NASAA and the International Federation of Organic Agricultural Movements (IFOAM).
- All companies provided product information to varying degrees of detail. Some gave brief descriptions and claims, while others gave chemical analyses of their products. Only two companies included ash in their analyses and none provided measurements of total acidity. Five companies provided Material Safety Data Sheets (MSDS) for their range of products.
- Three companies referred to trial results relating to their products but full details were not given. Of these, two provided graphs and a third, overall results from a trial with one of their products. Two companies mentioned projects with research institutions but, again, details were not given.
- Five companies used testimonials to promote their products including editorials, commercial newsletters and video clips of interviews with farmers.
- Only two companies attempted a detailed scientific explanation for the structure and function of humic substances. In each case the information and references given related to the macromolecular theories popular in the 1980s and 1990s. A third company explained the functions of humic substances without delving into questions of structure and a fourth described the mode of action of their humic products.

Product claims

By far the most 'scientific' information in the websites related to product claims, of which there were no shortages. They have been grouped and summarised according to physical, chemical and biological properties. Each company claimed many of the following properties for their products:

Physical properties

- Increased water holding capacity.
- Improved soil wetting.
- Promotion of good soil structure.
- Increased porosity of soil.
- Improved soil workability.

Chemical properties

- Increased cation exchange capacity. One company claimed a cation exchange capacity (CEC) for their product of 1400 (no units provided).
- Reduced leaching, improved retention and plant uptake of essential nutrients.
- Stabilisation of nitrogen and improved N efficiency.
- Complexation of phosphorus, forming stable phosphates.
- Increased penetration and retention of calcium in soil.
- Natural chelating/complexing agent – improved plant absorption of metal ions.
- Buffer against increased soil acidity from fertiliser use.
- Buffer against sodium, toxic chemicals and heavy metals.

Biological properties

- Plant growth regulator – auxin, gibberellin and cytokinin-like activity.
- Promotion of seed germination.
- Stimulation of cell division and growth, especially root growth.
- Increased microbial and enzyme activity.
- Increased cell permeability.
- Improved metal complexation, transportation and distribution in plants.
- Increased chlorophyll biosynthesis.
- Reduced stomatal conductance.
- Improved yield and drought tolerance.
- Anti-oxidant activity scavenging free oxygen radicals.
- Disease resistance.
- Fungal promotant, overcoming imbalances between fungi and bacteria in the soil.

Analysis of information

The claims made by manufacturers and sellers of humic products are very similar to the properties of humic substances. Before examining these however, the information provided by the companies raises some general issues.

Are humic products humic substances?

Humic products can be divided into two groups, those derived from brown coals and peats and those produced from organic residues such as composts. The peats and brown coals, lignites and leonardites contain various percentages of humic substances and are, therefore, a legitimate source (Hayes and Clapp 2001). However, products manufactured by chemical treatment of organic materials have not undergone the biological transformations that characterise the humic substances found in soils and their marketing as humic materials needs to be questioned. Many organic substances satisfy the functional definition of a humic acid, being soluble in alkali and precipitated by acid, yet cannot be classed as humic substances (Hayes and Clapp 2001).

Extraction and fractionation processes alter the chemistry and composition of humic materials, whether they are naturally occurring in soils or manufactured products from coals or organic materials. Studies of humic substances have only been made possible by the isolation and characterisation of fractions such as humic acids, fulvic acids and humins. These fractions may not even exist naturally in soils (Feller 1997) and may not be relevant to soil processes (Hayes and Clapp 2001).

Are humic products recalcitrant in soils?

The companies that provided a scientific rationale for their products based the information on the classical macromolecular models of humic structure. In these models the aromatic backbones of the molecules provide recalcitrance. There is some evidence that the aromatic structures in humic and fulvic acids are the product of chemical extraction procedures (Hayes and Clapp 2001) and do not exist in humic substances in nature. Although known for their molecular stability, aromatic compounds, in themselves, cannot resist microbial degradation. There is a similar problem with humic products derived from lignin. Lignin lasts longer on and in the ground than other plant compounds, but still gets degraded (Burdon 2001).

If the supermixture model of humic substances is correct, recalcitrance depends in the short term on the heterogeneity of the molecules and, in the longer term, on close associations with minerals within the soil. The main components of humic products are humic and fulvic acids and their salts. Given that they are, at best, fractions of humic substances, does sufficient randomness exist within their molecular structures to resist enzyme action? Do they retain the ability to aggregate into amphiphilic micelles and membranes with hydrophilic and hydrophobic parts? Can they form associations with minerals in the soil for long-term recalcitrance?

Stott and Martin (1990) calculated that humic substances in soil decompose at a rate of 2% to 5% per year with new humic material decomposing at a faster rate than old. Will additions of humic products be exposed to microbial attack and be decomposed before carrying out many of the functions for which they were applied? Although decomposition would render nutrients bound into the humic structure more available, are there cheaper sources per kilogram of nutrient?

Application rates and cost

For the most part, the application rates for the humic products surveyed were extremely low relative to the quantity of humic substances (HS) naturally available in Australian agricultural soils. At an average of 17 t HS/ha already in the topsoil, the addition of humate granules at 50 kg/ha represents only a 0.3% increase. This could only be viable if the humates were banded into the soil or combined chemically or physically with nutrients which they made more available. According to the product literature, liquid and foliar sprays are to be applied at even lower concentrations. Allowing for the dilution rates, the amount of humic product entering the soil would be negligible. Direct uptake by plants would be necessary for the products to have any benefit. The efficacy of nutrient-humate complexes and the absorption of humic molecules into plants are discussed in Section 4.

Broadcast of the "natural" humates at 200 kg to 1 t/ha provides product at rates that could have a benefit. Given that a porous soil with low organic carbon levels may have a humic substance content as low as 5 t/ha, adding an additional tonne as humic product may enhance soil quality. However, at a price exceeding $2,000/t, are there more cost effective ways of improving the soil, for example, mulching with composts?

Another issue arises in terms of application rates and costs. Humic substances cannot be purified (MacCarthy 2001). There is no definitive method for separating all of the non-humic material from humic molecules. Therefore, none of the products surveyed could contain 100% pure humic material. The companies surveyed advertised concentrations of humic acids in their products from 12% to 85% and fulvic acids as low as 0.16%. This lowers the amount of humic material being applied even more, relative to the quantity of humic substances naturally occurring in the soil.

Product quality

Most of the companies supplying humic products were at great pains to point out that there was an enormous variation in the quality of commercial humic materials and that theirs were, of course, the best. If quality refers to the quantity of humic and fulvic acids, then there is a wide variation in the quality of humic products. This is due to differing sources and manufacturing processes, such as isolation and pre-treatment methods. Unfortunately, there is also a lack of information relating to these issues across the industry (Iakimenko 2005). With no nation-wide registration or standardisation requirements, farmers only have the information supplied by individual companies on which to base their decisions.

The situation is complicated by the fact that there are still no internationally recognised extraction and analytical methods for humic substances. The humic acid content of a particular substrate will vary depending on the method of analysis. Fataftah *et al***.** (2001) determined the humic acid content of ten commercial products using three different analytical methods. Depending on the method used, the humic acid content varied from 87% less than that claimed by the manufacturer to over 800% more than the advertised content. Even the molecular weights can vary by an order of magnitude depending on the analytical method employed (Simpson 2002).

Conclusion

Based on the above evidence, it appears that companies selling humic products cannot reasonably promote them solely on the basis of their similarity to humic substances that exist naturally in the soil. Most of the information provided relates to activity in soils which may occur in the absence of the applied product. Claims of physical, chemical and biological benefits must stand on their own in the light of independent field trials and efficacy data. These will be examined in Section 4.

4. THE CLAIMS OF HUMIC PRODUCTS

Many claims have been made by the manufacturers and resellers of humic products about their benefits to agriculture. To a large extent these claims mirror the known properties of humic substances as they exist naturally in soils and are made on that basis. However, the question is not whether native humic substances are physically, chemically and biologically active in soils. Rather, what is under the spotlight is the ability of commercial humic products to provide additional agronomic benefit or a cost-effective solution for degraded soils and those low in organic matter.

Research into humic products

The body of published literature relating to humic substances is very large. Susic (2008) estimated that approximately 10,000 articles relating to humic substances, humic acids and fulvic acids have been published. The majority of this research has been devoted to the search for structure and the characterisation and function of humic substances as they occur naturally in soil and water.

Explaining specific interactions and processes and the behaviour of humic substances and commercial products on a larger scale is still hampered by the uncertainty surrounding their molecular structure (Kramer *et al*. 2001). The reactivity of humic substances is dependent on their structural and functional properties (Wang *et al*. 2001). Without adequate structural models it is difficult to interpret experimental data (Haberhauer *et al*. 2001). MacCarthy (2001a) expressed concern that, in their experimental design and the interpretation of data, researchers were ignoring the fact that humic substances are complex mixtures.

Published research into the efficacy of commercial humic products has been limited. The high expectations of the 1950s and 60s, when research was demonstrating the potential of products such as nitrogenous humic fertilisers, were not realised (Kline and Wilson 1994). Based on early, promising results, some companies extracted humic products from brown coals which were marketed aggressively with many miraculous claims. When these claims were not substantiated in the field, mistrust of humic products grew in the scientific and agricultural communities and research moved in other directions.

Research into the properties of naturally occurring humic substances continued with an indirect benefit for commercial products. Little attention has been paid to the analysis of untreated whole soil samples (Tan *et al*. 1992) due to the extreme difficulty in separating intact humic material from the mineral component of soils. Most work has been accomplished by extracting humic and fulvic acids from soils using alkaline solutions and other methods. This is a time consuming and expensive process. To ease the strain on staff and budgets, researchers turned to commercial humic products as their source material.

Malcolm and MacCarthy (1986) and Qiang *et al*. (1993) strongly advised against this practice. There were concerns about the lack of information regarding the origins, methods of extraction and pre-treatment of the commercial material. There was inconsistency in the analysis of samples from batch to batch from the same supplier. Malcolm and MacCarthy (1986) analysed seven commercial humic acid products. They were all distinctly different from soil or water humic substances and the authors concluded that no geochemical or environmental significance could be attached to any data obtained using them.

Despite the concerns, a body of research now exists through which commercial humic products have been tested for physical, chemical and biological properties. The research has been added to more recently with studies of commercial products in their own right. The warnings of Malcolm and MacCarthy (1986) and Qiang *et al*. (1993) should not, however, be ignored. The large discrepancy in analyses between samples and batches of a product mean that any extrapolation of results to a wider scenario should be undertaken with extreme caution.

Edmeades (2002) also suggested that determining the efficacy of a particular product from the published literature creates challenges. Only a small proportion of all research conducted is ever formally published. There is little incentive for researchers or scientific journals to publish non-significant or negative results. Therefore, a bias appears in the literature in favour of the products tested.

Another problem lies in the type of research conducted thus far. Most experiments involving humic extracts and products have taken place in the laboratory and glasshouse. The few published field trials have been mainly conducted with horticultural crops. Of 50 investigations reviewed for this report, 26 were laboratory experiments, 12 were pot trials and another four conducted in hydroponic solution. Only eight of the 50 studies were field trials. Very few investigations of commercial humic products have been undertaken in Australia.

Bowden (2004) emphasised the need for local soil test calibrations for the major nutrients, that is, fertiliser recommendation systems based on a large number of local trials. If local calibration of fertilisers of known and fixed analyses is required, how much more important is it for humic products which, by their very nature, are highly variable. To date, a sufficient number of field trials have not yet been conducted to provide farmers with any certainty regarding the performance of humic products.

Establishing quality parameters for humic products

Some companies do provide a limited analysis of their humic products. A more thorough physical and chemical analysis would provide additional useful information. Two measurements that are of particular importance are the acidic functional groups analysis and the percentage ash content with the elemental analysis of that ash (Varshovi and Sartain 1993).

As with humic substances, the reactivity of humic products is largely due to the high number of aromatic and aliphatic carboxyl (COOH) and phenolic (OH) functional groups. Hydrogen ions dissociate from these groups leaving many net negative charges across each molecule. The higher the measurement of total acidity, COOH and phenolic OH groups, the more reactive the product will be.

A review of the scientific literature uncovered functional group analyses for ten commercial products containing humic acids (Table 4). Total acidity ranged from 2.4 to 8.6 meq/g with a mean of 4.9 meq/g. This was lower that that measured for humic acids extracted from 15 brown coals with a mean total acidity of 6.7 meq/g (range = 4.9 – 9.8 meq/g). None of the Australian companies selling humic products surveyed for this report provided functional group analyses on their websites.

High ash contents, especially those comprising aluminium and iron ions and clay minerals will block the functional groups (Varshovi and Sartain 1993). The cations form bonds at the negative sites and the clays complex with the humate. Therefore, a low ash content is desirable unless the product is being sold specifically as a source of plant nutrients. Ash contents for 26 commercial products published in the literature ranged from 2.7% to 32.8% with a mean of 18.5% on a weight basis (Table 2). Two of the surveyed Australian manufacturers provided ash analyses for some of their humic products.

As useful as these analyses are they are time-consuming and expensive, adding to the cost of the product. Also, the results will vary depending on the method of analysis (Fataftah *et al*. 2001). Until standard analytical techniques are established and adhered to internationally there can be no certainty as to the quality of commercial humic products.

With these research and analytical limitations in mind, a review of the literature relating to commercial humic products is provided in this section and the product claims assessed against the available data. The mechanisms underpinning the physical, chemical and biological properties of these products are also discussed.

Plant growth and yield

Numerous studies have been undertaken on the effects of humic substances and commercial humic products on plant growth and yield. Chen and Aviad (1990) have provided a comprehensive and often cited review of the work accomplished before 1990. The papers reviewed demonstrated a positive response of germination and seedling growth, root initiation and growth and shoot development to a range of humic extracts from a variety of sources. Water absorption, respiration and germination were all augmented in a variety of seeds including winter wheat, maize and barley. The rate of germination responded to humic treatments but not the percentage of viable seeds.

From the papers reviewed by Chen and Aviad (1990), it seems that root growth is more enhanced than shoot growth by the addition of humic extracts. The length and weight of roots increased with treatment, as did the development of secondary and lateral roots. Foliar applications, as well as soil/medium applications, were found to have a positive effect on root growth. There was some evidence that fulvic acids may be more effective than humic acids. Responses were found to increase with application rate to a certain point and then decrease at higher concentrations.

Shoot development, though not as responsive to treatment as root growth, also increased with humic treatments (Chen and Aviad 1990). Application rates for humic and fulvic acids of 25 to 300 mg/L added to nutrient solutions or 50 to 300 mg/L as a foliar spray were found to be effective. In sand or soil cultures optimum levels were 400 to 800 mg/kg soil for root and shoot growth.

Karr (2001) has provided a more current review with studies undertaken before 2001. He concentrated on responses to oxidised lignites and their extracts. Similar results to those of Chen and Aviad (1990) were found with humic treatments stimulating root and shoot growth. Numerous authors including Nardi *et al*. (2002), Jones *et al*. (2007) and Çelik *et al*. (2008) have provided a brief review of the literature relating to plant growth effects as introductions to their own research.

The major limiting factor of these studies is that most were conducted under controlled laboratory conditions or in glasshouses. The majority used seedlings or young plants in nutrient solutions, growth media or in pot trials. Many were vegetable crops. Extrapolating these results to agricultural conditions is fraught with difficulties. Another challenge is that the reviewers, by and large, only included studies that had shown a significant response to humic products.

Karr (2001) did review a handful of field trials. Positive responses from treatment with humic products were recorded for tomatoes, cotton, grapes and sweet potatoes. The problem is that the little field work that has been done is scattered around the world under different conditions using a variety of crops. Humic products have been extracted from a number of sources and applied using several methods and a wide range of application rates. There is no repeatability.

A sample of 20 studies on the effects of humic products on plant growth has been reviewed as part of this report. The results are summarised in Table 5. Once again, the work has mostly focused on hydroponic and pot trials, many conducted in North America. Of the nine pot trials, six used local soils as the growth medium. The other three used either acid washed sand or a soil-less bedding plant medium. There was a significant increase in shoot and/or root growth of plants grown in the soil-free media treated with a humic product. Three of the trials using soil showed an increase in growth and in the other three there was no significant difference. However, the sample size is too small and the factors of crop and soil type, humic product and application rate are all too variable to draw any conclusions from these results.

Another limiting factor is product quality. The efficacy of humic products depends largely on the application of correct rates of solutions of known concentrations (Chen and Aviad 1990). However, given that there is a large variation in the humic or fulvic acid content of a product depending on the method of analysis (Fataftah *et al*. 2001), uncertainty as to the actual humic content of any product will continue to exist until there is some standardisation of extraction and analytical techniques.

Figure 11 - A field trial of a humic product on a kikuyu pasture on the Mid North Coast of New South Wales. There were no significant results.

Most of the authors of the 20 reviewed studies suggested mechanisms by which the humic products might be stimulating plant growth. Improved nutrient availability and uptake, metal chelation, increased water efficiency, enhanced cell membrane permeability, antioxidant and hormone-like effects and improved microbial metabolism were all mooted as possibilities. Some of the studies concentrated on the measurement of plant growth, citing other work as evidence supporting the proposed theories. Several researchers tested their hypotheses with measurements of nutrient release rates, plant tissue tests, antioxidant and hormone analyses, microbial activity and infrared (IR) and NMR analysis.

There is evidence that both humic substances in soil and amendments with humic products can promote plant growth by both direct and indirect mechanisms (Celik *et al*. 2008). Indirectly, humic materials improve soil structure and water holding capacity and increase the solubility and uptake of macro and micronutrients. There is also a direct effect on the physiological and biochemical processes of plants and microorganisms in the soil. The following sections will explore the physical, chemical and biological claims of the manufacturers of humic products to determine their veracity.

Table 5 - Studies on the effects of humic products on plant growth

Note - Unless otherwise stated, nutrients were applied to the crops to meet agronomic needs. The results column shows the most effective treatment applied.

Author	Year	Location	Type of trial			Crop	Humic product	Application rate	Results	Suggested mechanisms
			Lab	Pot	Field					
Arancon	2006	USA		✓ Soil-free media		Marigolds	Vermicompost HA Commercial HA	250 – 1000 mg/kg	Increased root weight, tomato weight and number of strawberries	Improved MO metabolism and nutrient uptake. Hormone action
Atiyeh *et al*.	2002	USA		✓ Soil-free media		Capsicum	Vermicompost HA	50 – 500 mg/kg	Increased plant height, leaf area, shoot and root dry weight	Hormone-like activity
Ayuso *et al*.	1996	Spain	✓			Strawberries	Leonardite HA Peat HA	< 10 mg C/L	Increased top growth	Improved nutrient uptake
Berkowitz *et al*.	1970	Canada		✓ Soil		Tomatoes	Nitrogen enriched coal	100 ppm N	NSD cf. control	Slow release of N
Bronwell *et al*.	1987	USA			✓	Cucumbers	2 commercial leonardites	10 – 20 L/ha	Grapes – increased harvest by 25% over 5 years Olives – new growth flowering with 67 – 125% increase in mature fruit Tomatoes – unusual growth patterns with yield increases Cotton – increased boll retention	N/A
Celik *et al*.	2008	Turkey		✓ Soil		Barley	Leonardite	1 g HA/kg soil	Increased maize growth in soil treated with $CaCO_3$	Increased solubility of plant nutrients
Cimrin and Yilmaz	2005	Turkey		✓ Soil		Red canary seed	HA	300 kg/ha	NSD – Head weight of lettuce HA × P increased N content of lettuce	Increased P availability
Clapp *et al*.	1998	USA	✓			Grapes	Peat and leonardite HA	10 – 50 mg/L	Increased root and shoot growth by 13 – 31%	Stimulation of root cell elongation and proliferation

Author	Year	Location	Type of trial			Crop	Humic product	Application rate	Results	Suggested mechanisms
			Lab	Pot	Field					
Eyheraguibel *et al*.	2008	France	Hydroponics			Olives	Ligno-humates	50 mg C/L	NSD – germination Increased root elongation, root, shoot and leaf biomass	High water efficiency and nutrient uptake
Figliolia *et al*.	1994	Italy			✓	Wheat	Peat HA	16 & 32 kg HA/ha No fertiliser	Initial proliferation of roots/shoots and increased growth but lower end yield than control	Physiological effect on plant
Jones *et al*.	2007	USA		✓ Soil		Spring wheat	HA coated on MAP	1.7kg/ha	NSD in P availability, Fe & Zn uptake, shoot biomass or grain yield	N/A
Lobartini *et al*.	1992	USA		✓ Acid washed sand		Maize	Commercial & soil HA	10 ml 50 ml	Increased growth of maize: 10 ml commercial HA = 50 ml soil HA	N/A
Lobartini *et al*.	1994	USA	Hydroponics			Corn	Soil-derived HA	800 mg/L	Apatite + HA at pH 5 increased plant growth significantly	Increased P availability
Lobartini *et al*.	1998	USA	Hydroponics			Corn	Soil-derived HA	400 mg/L	DW of corn with $FePO_4$ + HA = DW of corn with KH_2PO_4	Increased P availability
Mackowiak	2001	USA	Hydroponics			Spring wheat	HA	1.0 mmol	NSD in total biomass or seed yield when compared with synthetic chelate	Metal chelation
O'Donnell	1973	Canada	✓			Pelargonium	0.05%	0.05%	Proliferation of roots	Auxin-like effect
Selim *et al*.	2009	Egypt			✓	Potatoes	N/A	N/A	HS + NPK increased tuber yield by 16.47% cf. NPK alone	Improved NPK uptake
Valdrighi *et al*.	1996	Italy		✓ Soil		Chicory	1000 mg/kg	1000 mg/kg	Increased growth	Enhanced cell membrane permeability
Van Dyke	2008	USA			✓	Bent grass	HA	9 kg/ha	NSD in top growth. Increased root depth	N/A
Zhang and Ervin	2004	USA		✓ Soil		Bent grass	HA and seaweed extract	1.5 kg/ha	HA + seaweed increased root mass by 21 – 68%	Hormone-like effects

Abbreviations: cf. – compared with; DW – Dry weight; FA – Fulvic acid; HA – Humic acid; HS – Humic substance; MAP – Monoammonium phosphate; MO – Microorganism; N/A – Not available; NSD – No significant difference

Claims of physical properties

Many commercial humic products are marketed with the claim that they will promote good soil structure and, therefore, improve other soil physical properties such as porosity and water holding capacity.

Soil structure

Background

There is a world-wide concern about the loss of organic matter in agricultural soils and, with it, the deterioration of soil structure. Albiach *et al*. (2001) attributed the decline in Europe to intensive cropping systems that do not return adequate quantities of plant biomass to the soil.

In Argentina, Bongiovanni and Lobartini (2006) measured a reduction of 92% in the large macro-aggregate content of tilled versus undisturbed soils. They hypothesised that, as macro-aggregates were destroyed, the humic substances would be exposed to attack from microorganisms and be degraded. A measured reduction in native humic and fulvic acid contents by 40 to 70% in tilled soils supported this suggestion.

In Victoria, Australia, Imbufe *et al*. (2005) discussed the compounding problem of repeated wetting and drying cycles from seasonal weather patterns and irrigation. Continual swelling and shrinkage fractures the macro-aggregates in some soils. The remaining micro-aggregates become more susceptible to dispersion and erosion, resulting in increased slaking, reduced water infiltration, erosion and loss of productivity. Piccolo *et al*. (1997b) encountered the same problem in Italy. They studied the effects of repeated wet-dry cycles in naturally well-aggregated soils and measured the ensuing structural collapse.

In Western Australia, Yamaguchi *et al***.** (2004) were facing a different cause of structural decline. Salt encroachment into the kaolinite-quartz wheatbelt soils was reducing aggregate stability. The land, in many cases, was not responding to the traditional calcium amendment, mainly in the form of gypsum.

These problems led the researchers cited above to trial commercial humic products as soil conditioners that might improve aggregate stability. The stability of soil aggregates is influenced by the quantity and quality of organic matter in the soil (Piccolo and Mbagwu 1999). Bulk organic residues, such as manures and composts are often used to amend degraded soils. The advantages and disadvantages of composts for soil amelioration and the economics of such use have been well reviewed in the literature (Cameron *et al***.** 1997; Chan *et al***.** 2008; DECC 2008; Gibson *et al***.** 2002). Gibson (2002) noted that distance from the source could be a decisive factor in the use of organic residues due to transport costs.

What was needed was a soil conditioner that would act rapidly at low application rates (Piccolo *et al***.** 1997b). Synthetic polymers, such as polyacrylamides and polyvinyl alcohols were found to be effective at low rates but were expensive (Burdick 1965) and easily degraded by micro-organisms (Piccolo *et al***.** 1997b). As their effects were transient, repeated applications were necessary, which was a costly exercise.

Product claims

Humic materials, produced from low-grade coals, were seen as a promising alternative to bulk organic residues and synthetic polymers. These humic products were relatively inexpensive, there was potentially an unlimited supply, they were free from pollutants and were both highly reactive yet recalcitrant. Manufacturers are quick to point out the merits of their products in relation to improved soil structure.

How does it work?

The mechanisms by which humic substances and commercial humic products stabilise soil are not well understood. Stevenson (1994) suggested that several types of bonds may be involved including electrostatic interactions, hydrogen bonds, van der Waal's forces, hydrophobic bonding and ligand exchange. Conflicting reports in the literature, supporting one or another mechanism, may be due to different mechanisms acting in different situations (Piccolo and Mbagwu 1999).

A commonly accepted explanation is that humic substances form complexes with clays via polyvalent cations that act as a bridge, or chelate, between the two (Figure 12). The carboxylic and phenolic-OH functional groups dissociate leaving multiple negative charges on the humic molecule (Imbufe *et al.* 2005). Polyvalent cations, especially Al^{3+}, Fe^{3+} and Ca^{2+}, bond with the negative charges on the humic molecule and those on the clay surfaces (Stevenson 1994).

Tugulea *et al*. (2001) demonstrated the adsorption of humic and fulvic acids onto mica particles. The size of the aggregates increased both with increasing ionic strength and decreasing pH. Their results suggested that ionic strength may be more important than pH in the complexation of humic material within the clay fraction of soils.

A further mechanism protects these humic-metal-clay complexes from the action of water. Humic substances can aggregate into micelles and films with hydrophilic and hydrophobic parts (Piccolo and Mbagwu 1999). The hydrophilic end, the negatively charged functional groups, strongly adsorb to the metal-clay complex forming the interior of soil micro-aggregates. The hydrophobic exterior forms a water repellent coating, reducing infiltration into the micro-aggregate (Figure 12).

Electrostatic interactions –

Large molecules can develop some areas of positive electric charge and other areas of negative electric charge. Electrostatic fields occur as these positive and negative fields develop and interact with each other and similar fields on other molecules.

Hydrogen bonds –

Hydrogen atoms attached to a molecule can develop a net positive charge attracting them to electronegative atoms such as nitrogen, oxygen and chlorine. They form relatively strong bonds between different molecules or different chemical groups on the same molecule.

Hydrophobic bonds/forces/ interactions –

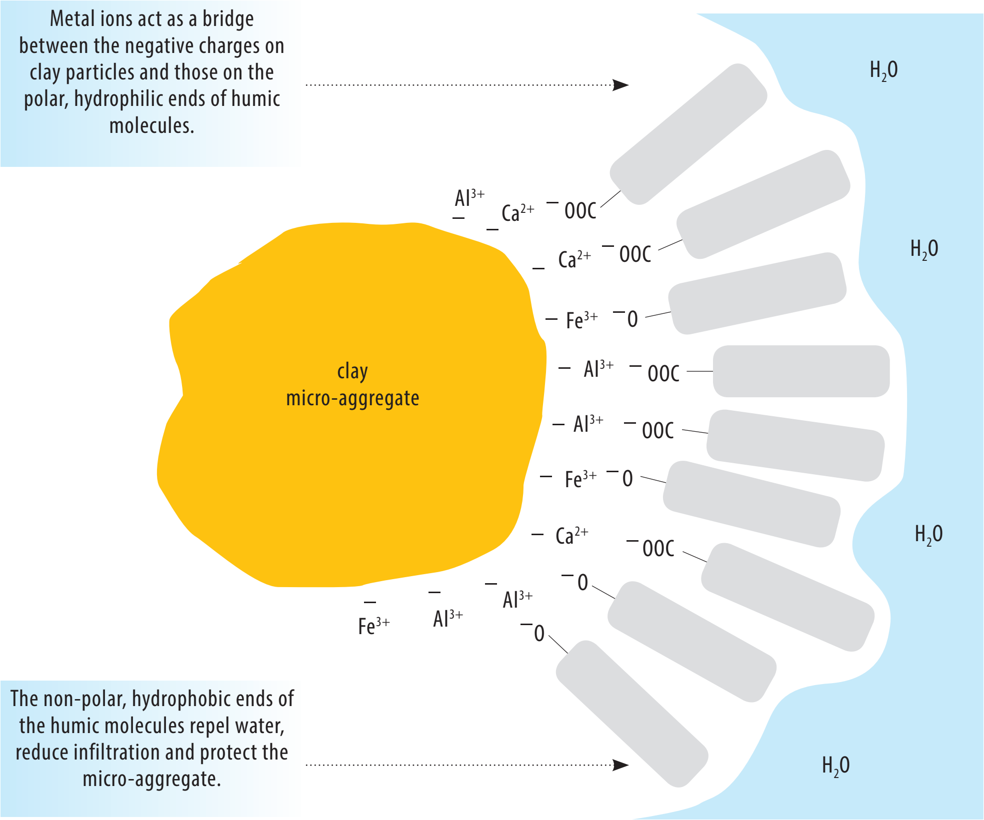
Molecules that have no net electric charge are non-polar and hydrophobic, or water-fearing. As they repel water, the individual hydrophobic molecules tend to clump together.

Ligand exchange –

Polyvalent cations such as calcium (Ca^{2+}) and aluminium (Al^{3+}) can form multiple bonds with functional groups on macromolecules. These functional groups, known as ligands can be replaced by other groups in a process known as ligand exchange.

Van der Waal's forces –

Electrons are continually orbiting around the nuclei of atoms. At any point in time there are likely to be more electrons on one side of an atom or molecule than on the other side creating a temporary dipole – one side is more electrically positive and the other side more electrically negative. A temporary dipole in one molecule can induce another temporary dipole in a neighbouring molecule and so on. A whole lattice of molecules can be held together in a solid using van der Waal's forces.



Metal ions act as a bridge between the negative charges on clay particles and those on the polar, hydrophilic ends of humic molecules.

The non-polar, hydrophobic ends of the humic molecules repel water, reduce infiltration and protect the micro-aggregate.

Figure 12 – Conceptual diagram of complexes that can form between humic molecules and clay particles, protecting the structure of micro-aggregates

Where's the evidence?

Laboratory studies into the effects of humic acid (HA) and fulvic acid (FA) on soil aggregate stability have been promising. Piccolo *et al*. (1996) measured a 40% to 120% improvement in the aggregate stability of severely degraded arid to semi-arid Mediterranean soils with low application rates of a coal-derived humic acid (0.05 – 0.10 g HA/kg soil). Further studies (Piccolo *et al*. 1997b) on the interaction of humic acid and wetting/drying cycles on soils again resulted in a significant improvement of aggregate stability at low application rates equivalent to 100 to 200 kg HA/ha. The disaggregating effects of the wet/dry cycles were also substantially reduced with the humic acid treatment.

In a similar study, Imbufe *et al*. (2005) compared the effects of various rates of a commercial potassium humate on the aggregate stability of an acid soil from the Yarra Valley and an alkaline sodic soil from the Goulburn Valley, Victoria. Significant increases in mean-weight diameter (MWD) of the acid soil aggregates were measured at low treatment rates although the sodic soil required 1 g HA/kg soil (2 t/ha) for a significant improvement (Imbufe *et al*. 2005). However, after seven wetting/drying cycles the MWD declined with the humate treatment.

The effects of calcium additions were compared with humic acids derived from peat and lignite in sodic West Australian soils (Yamaguchi *et al*. 2004). Only calcium formed micro-aggregates in a kaolinite-quartz mix. Lignite-derived HA amplified the effect with 30% of the smaller particles forming larger aggregates. The peat HA had little effect despite its chemical similarity to the lignite HA. Neither humic acid had any effect when sodium was introduced into the kaolinite-quartz mixture. When the actual sodium-affected wheatbelt soils were tested, calcium had no aggregating effect. Peat HA was more effective than lignite HA in acid conditions (pH = 4.5). The aggregating effect of humic acid increased with increasing clay content of the soil.

Piccolo and Mbagwu (1999) removed the native organic matter from a Typic Haplustalf to approximate the loss of organic matter from agricultural soils. In controlled laboratory experiments they compared the action of a polysaccharide gum, stearic acid and humic acid on the soil with and without organic matter. Removal of organic matter led to a rapid reduction in aggregate stability by 40%. The effect of the gum was transient and diminished rapidly. Stearic acid slowly improved aggregate stability. At 0.2 g HA/kg soil (400 kg/ha) humic acid increased aggregate stability by 27% in the soil without organic matter and by 73% in the soil with organic matter. Piccolo and Mbagwu (1999) suggested that the hydrophobic parts of both the native organic matter and added humic acids might interact to improve aggregate stability.

With no reports in the literature in which the stabilising effects of humic acids had been tested under natural or simulated rainfall, Piccolo *et al*. (1997a) conducted a rainfall simulation trial. A loam and a silty loam were packed into erosion/drainage boxes and tested with a coal-derived humic acid at various rates. The loam was severely compacted and the silty loam was a dispersing, low porosity soil with salinity and crusting problems. The simulator provided 40 mm of rainfall over a one hour period. At 100 kg HA/ha, soil loss was reduced by 36% in the silty loam. The same reduction in soil loss was achieved in the loam at 200 kg HA/ha. Amendment with humic acids at 200 kg/ha delayed runoff initiation by 15 minutes in the loam but only by six minutes in the silty loam. The delay in runoff initiation combined with accelerated drainage accounted for 58 to 81% of the reduction in erosion. No other amendments were compared with humic acids in this trial.

With promising data from laboratory and rainfall simulation experiments and a mechanism supported by research, the next logical step should be field testing to verify whether humic acids can improve soil aggregate stability. Here, however, the literature is lacking. Measuring small but significant changes in the structural stability of soils in the field is very difficult due to the many complex processes occurring in soils and the wide range of variables involved. Only one field trial on the topic was found during the literature search for this project.

Albiach *et al*. (2001) conducted a 5-year field study of organic amendments applied to a sandy-silty loam with an organic matter content of 1.25% and pH of 8.18. Five organic amendments: compost; sewage sludge; manure; a vermicompost; and a commercial humic acid solution were trialled. After five years of applying the humic acid at the recommended rate of 100 L/ha/year, there was no significant change in organic matter, total humic substances, humic acids, carbohydrates or microbial gums in the soil compared with the control. The compost, sludge and manure, all applied at 24 t/ha/year, increased all of the above parameters significantly. Albiach *et al*. (2001) concluded that, due to the high cost of the commercial humic acid, the manufacturers had recommended applications at unrealistically low rates to attract sales.

Potential or presumption?

Most of the manufacturers surveyed for this report set their application rates well below those that achieved significant results in the laboratory studies described above. For commercial humic products to be considered as potential soil amendments, field trials will need to be conducted at rates that have been shown to be beneficial and a cost-benefit comparison with other amendments carried out. Alternatively, long-term studies using the lower application rates that are currently recommended should be commenced to measure potentially small, incremental changes.

Water holding capacity

Background

If commercial humic products can improve soil structure, it should follow that they will have an effect on soil water properties. The formation of micro and macro-aggregates should improve porosity and, hence, water holding capacity. In the 1960s the purported ability of humates to regulate water holding capacity was considered to be their most important contribution to agriculture (Burdick 1965).

Product claims

Many companies today sell humic products with claims of improved soil wetting and increased water holding capacity.

How does it work?

Depending on the pH, ionic concentration and presence of neutral salts, humic and fulvic acids can act as colloids dispersed in the soil solution (Stevenson 1994). When they form micelle-like aggregates as shown in Figure 13, with hydrophobic interiors and hydrophilic exteriors, the "water-loving" surface of the micelle attracts and holds water (Wershaw 1986). One manufacturer of commercial humic products described the process of dropping a sample of dry humic acid into water. It swelled to several times its original size, forming a jelly-like substance. However, this demonstration is somewhat misleading as it does not take into account all the forces or tensions acting on water in a soil.

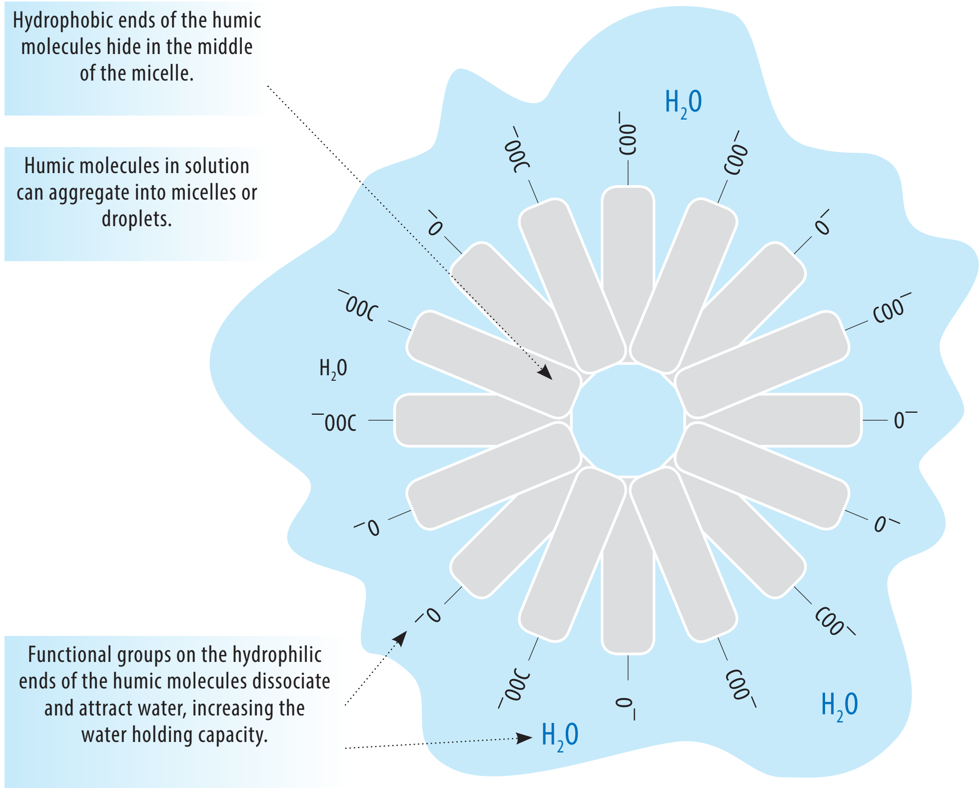


Figure 13 – Conceptual diagram of a humic micelle with the hydrophobic ends hidden in the interior and the hydrophilic ends attracting and holding water molecules

Where's the evidence?

Available water holding capacity is a common measure that can be determined in the field or laboratory (Craze and Hamilton 1994). However, few studies have been made of the possible association between humic products and soil moisture availability (Van Dyke 2008).

Piccolo *et al*. (1996) carried out laboratory studies into the effect of humic acid on water retention in three severely degraded Mediterranean soils from agricultural sites. They demonstrated that coal-derived humic acids at 0.05 g HA/kg soil (100 kg/ha) significantly increased field capacity and permanent wilting point. Available water capacity increased by an average of 22% across the three soils. At the time of this study there was no direct evidence that the results might be repeated in the field.

In their erosion study under a rainfall simulator, Piccolo *et al*. (1997a) attributed the reduction in run-off erosion with humic acids at 100 kg HA/ha more to improved water retention capacity than to aggregate stability. However, they only measured time to initiate run-off and drainage, not the available water holding capacities of the treated and control soils.

Van Dyke (2008) studied the effect of humic acids applied at commercial rates to putting greens. Rather than increasing the moisture retention of the soil, humic acid treatment significantly decreased soil volumetric water content and dried down the root zone. Treated putting greens required more frequent watering than the control greens. Van Dyke (2008) suggested that the humic acids may have adsorbed to the soil mineral surfaces and increased the water repellency of the soil surface layers.

Potential or presumption?

It appears that the amphiphilic nature of humic molecules, having hydrophilic and hydrophobic parts, can potentially both attract and repel water. If the humic molecules self-aggregate into micelles, the hydrophobic parts will be "hidden" in the interior of the micelle and the hydrophilic exterior will attract water, thus increasing the water holding capacity of the soil (Figure 13). If, however, the humic molecules form humic-clay complexes, they will organise into a film on the clay surface with their hydrophobic parts exposed to the soil solution (Figure 12). Water will be repelled from the micro-aggregates, potentially decreasing the wettability and water holding capacity of the soil.

The soil conditions under which each scenario is most likely to occur need to be determined in the laboratory and tested in the field. Until more data is available it would not be prudent to recommend humic products on the basis of their ability to improve the water retention of soils. Also, given the wide variability in the chemical analyses of humic products, each would need to be tested under a variety of soil conditions before claims of improved soil water conditions could be made.

Claims of chemical properties

pH Buffer

Background

The ability of humic substances to exhibit buffering capacity over a wide range of pH values is commonly accepted and has been established in the literature since the early 1900s (Stevenson 1994). Soils that have a high humus content are, in general, well buffered.

Product claims

Manufacturers of humic products commonly claim that their particular formulation will buffer soil pH, especially against the acidifying effects of fertilisers. These claims are based largely on the buffering properties of native soil humic substances.

How does it work?

Acidic functional groups attached to the humic molecules, especially carboxylic (COOH) and phenolic-OH groups, provide this buffering capacity as shown in Figure 14. The COOH groups dissociate in acid soils from pH 4 to 7 (Stevenson 1994). Phenolic-OH groups dissociate in alkaline soils above pH 8. Between pH 7 and 8 there is an overlapping zone where ionisation of both groups occurs. The resulting anionic regions of the humic molecules act as weak polyelectrolytes. Charges on the molecules are determined by the pH of the soil solution and the presence of neutral salts. In simple terms, if the pH falls, H^+ ions will bond with the COO^- and OH^- anions raising the pH but reducing the cation exchange capacity. The opposite occurs if soil pH increases.

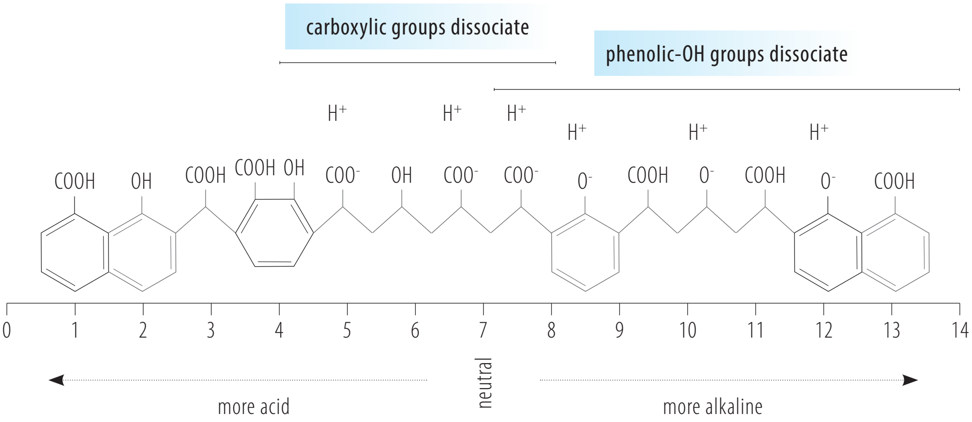


Figure 14 - The effect of soil solution pH on the buffering capacity of humic molecules

Humic and fulvic acids themselves can not raise the pH of a soil. The cation exchange sites on a humic or fulvic acid will be saturated with hydrogen ions (Mikkelson 2005). When added to the soil these H^+ ions will dissociate from their functional groups, lowering the pH of the soil solution.

To be effective as pH buffers, the products need to be in the form of a salt, or humate, with the exchange sites dominated by a cation other than hydrogen. Examples are calcium, potassium or sodium humates. The small size and high charge density of H^+ ions place their adsorption strength between that of Al^{3+} and Ca^{2+} (Tisdale *et al.* 1993). When the humate enters the soil solution, H^+ ions replace the Ca^{2+}, K^+ or Na^+ ions on the exchange sites of the humic molecules, thus raising the pH of the soil. Depending on the quantities, this could lead to greater leaching of nutrients as the cations are released into the soil solution.

Adsorption strength –

The strength with which cations are held onto clay and humic colloids in soil. The adsorption strength of a cation increases with its electrical charge and decreases with its size to give the series: $Al^{3+}>H^{+}>Ca^{2}>Mg^{2+}>K^{+}=NH^{4+}>Na^{+}$

This problem is compounded by the lack of regulations relating to the labelling of humic products and their contents. A farmer who is considering trialling one of these products is relying on the manufacturer to accurately label it as a humate or acid, regardless of the claims made of its efficacy.

Where's the evidence?

There is little reference in the literature to trials conducted with commercial products. Most column studies are done with single organic acids or low molecular weight acids due to the need for a product that is water soluble and easily carried down the column (Peiris *et al.* 2002).

Peiris *et al.* (2002) did investigate the effects of calcium humates and fulvates on an acid red podzol from the Riverina district of New South Wales. They were looking for a soil amendment that would act more quickly than lime on root zone pH. The humic products and lime were applied at a rate of 160 g Ca/m^2 (4 t lime/ha) to the surface of columns of the soil which had a pH of 3.8 and an aluminium content of 7.7 mmol/kg. The fulvate had a higher total acidity and lower molecular weight than the humate.

Relative to the control, the Ca-fulvate raised the soil pH to an average of 5.0 in the top 15 cm. It lowered the exchangeable aluminium with 90% of the lost Al recovered in the leachate. Iron was also leached by the fulvate. There was a smaller increase in pH with the Ca-humate to 4.5 and only 65% of the exchangeable Al was lost in the leachate. More of the Al was converted to an immobile form, complexed with the Ca-humate. Given the short duration of the experiment, lime had no effect on either the pH or exchangeable Al content of the soil.

Peiris *et al***.** (2002) concluded that, although the Ca-fulvate had a more pronounced effect than the Ca-humate on soil pH, its high complexing ability and solubility could increase the podzolisation of the soil, transporting nutrients below the root zone. The higher molecular weight humates showed more promise as an alternative soil ameliorant to lime. There is, however, a risk that the added humates could ameliorate the surface but push the problem to depth if the aluminium is not deactivated.

Potential or presumption?

Recommended broadcast application rates of most humic products range from 10 kg/ha to one tonne per hectare. Given that there are already 17 t/ha of native humic substances in the average Australian agricultural soil, these application rates would increase the total content by 0.6% to 6%. Compared to the natural buffering capacity of the soil, these low application rates can only have a short-term effect on soil pH and that, only in the area immediately adjacent to the application site.

Of course, nothing is simple with humic materials and the anionic groups that buffer pH can become involved in a wide range of reactions with other anions, cations, organic molecules, clay particles and microbial and plant cells. Therefore, it is not possible to predict how the addition of a certain quantity of humic product will affect soil pH even if its quality, as a measure of the total acidity of the product, is known.

Although the positive results of Peiris *et al***.** (2002) are encouraging, more tests with a wide range of soils need to be conducted and replicated in the field, with appropriate cost-benefit analyses, before commercial humates and fulvates can be recommended as an alternative treatment for acid soils.

Cation Exchange Capacity

Background

Organic matter, including the humic fraction, contributes from 25 to 90% of the total cation exchange capacity (CEC) in the A horizon of mineral soils (Stevenson 1994). CEC depends on the nature and relative amounts of the clays and organic matter as well as the pH of the soil solution. Total acidities for humic molecules range from 485 cmol/kg for humic acids to 1,400 cmol/kg for fulvic acids. This compares with 3 to 5 cmol/kg for kaolinite and 150 cmol/kg for both montmorillonite and vermiculite (Stevenson 1994).

Product claims

As with pH buffering capacity, a common selling feature of commercial humic products is their presumed ability to improve cation exchange capacity in soils. Claims are made based on the contribution of native soil organic matter, and especially humic substances, to CEC.

How does it work?

It is the ionisation of carboxylic (COOH) functional groups on the humic molecules that provide most of the negative charges (COO^-) for cation exchange (Stevenson 1994). The surfaces of humic molecules have a net negative charge at all pH values in which plant growth occurs (Mikkelson 2005). Bonds form between the anionic groups on the humic molecules and cations in the soil solution (Figure 15). The strength of cation adsorption is dependent on the valency of the cation and its bonding energy. Many series have been proposed showing the relative strength of ionic bonds between cations and anionic surfaces, such as the following example by Stevenson (1994): $Fe^{3+} \approx Al^{3+} > H^+ > Ca^{2+} > Sr^{2+} > Mg^{2+} > K^+ > Na^+ > Li^+$

Bond energy –

A measure of the strength of a chemical bond between atoms or ions in a compound. The higher the bond energy, the harder it is to break the bond and the more stable the compound.

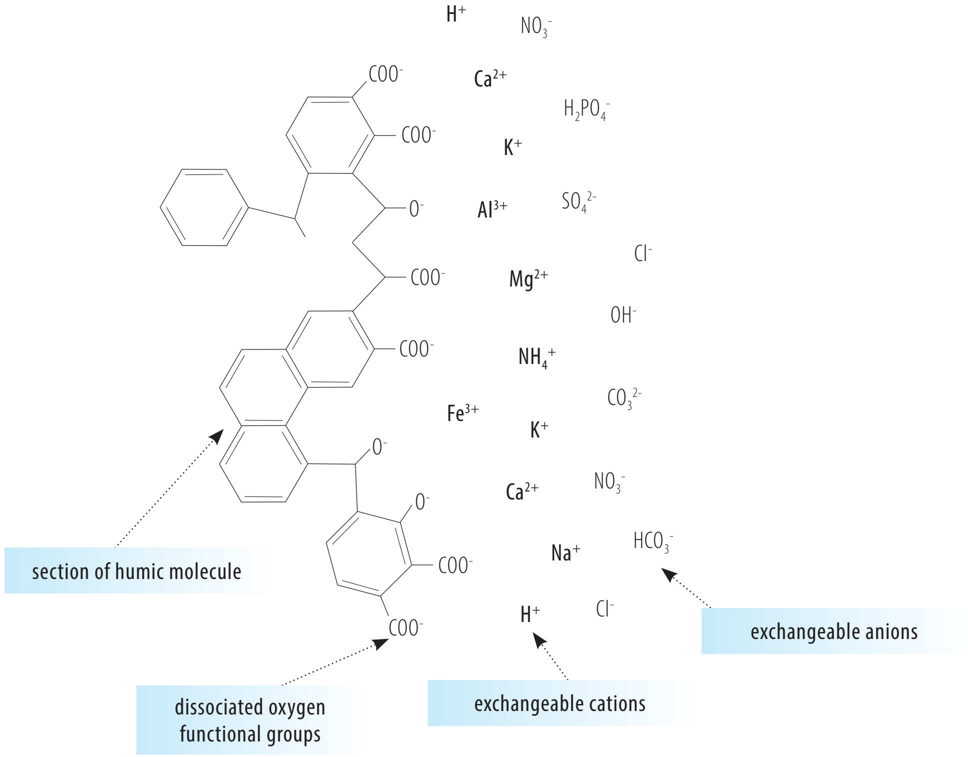


Figure 15 - Cation exchange on humic molecules occurs when oxygen functional groups dissociate, leaving a net negative charge on the surface of the molecule. Cations are adsorbed onto these negative charges and, in turn, attract exchangeable anions in the soil solution.

If clay particles are also involved there is a rearrangement of the series depending on the type of clay (Varadachari *et al*. 1991). The ability of humic molecules to bind to cations is fundamental to their capacity to chelate micronutrients and heavy metals. This will be discussed in the section on metal chelation.

Where's the evidence?

The measured effects of commercial humic products on the cation exchange capacity of soils are poorly represented in the scientific literature. Despite the breadth of research that exists relating to humic materials, there are virtually no references to trials conducted with humic products or extracted humic substances on cation exchange.

Potential or promise?

In terms of CEC, the problem facing commercial humic products is their recommended application rates and cost. Kussow (1994) calculated the effect of a commercial humic acid claiming to have a CEC of 500 – 600 meq/100 g. Adding 2 lb/cubic yard (1.2 kg/m^2 or 12 t/ha) of the humic acid to an 80:20 sand-peat root zone mix would raise the CEC by only 0.37 meq/100 g of medium at substantial cost. At the low application rates recommended by Australian suppliers of commercial products, the results in agricultural soils would either be negligible, very expensive or both.

This should not rule out product trials relating to CEC. If companies are claiming benefits they should be verified. There may be a role for humic products in soils with inherently low CEC and nutrient status. Significant results might also be obtained by strategically banding the product with fertiliser or seed where a small application rate can have a relatively large effect. Comparisons should be made with other soil amendments, especially organic residues and lime.

For any trials to be relevant certain protocols should be put in place. The average and total acidities should be measured for each product tested and appropriate soil analyses carried out before and after the trial. After all, a humic product does not enter a paddock soil with the label "For cation exchange only"! The same functional groups that are responsible for CEC could also be buffering soil pH, complexing with clays via metal chelates or hydrating to improve the water holding capacity of the soil.

Nitrogen

Background

More than 50% of the nitrogen in soils exists as a structural component of humic substances and is not readily available to plants (Stevenson and He 1990). Depending on the extraction method used, the nitrogen content of humic acids ranges from 1 to 4% (Stevenson 1994). Nitrogen is extracted as amino acids, amino sugars, ammonium and acid-insoluble N. It occurs in humic substances as amino acids attached to aromatic rings, bridges between quinone groups, parts of heterocyclic rings, open chains and peptides and proteins. A significant proportion of nitrogen in humic substances exists in an unknown form designated as the HUN [hydrolysable unknown-N] fraction.

Quinone –

A class of organic compounds derived from aromatic units such as benzene where an even number of C-H groups are converted into C=O groups.

Heterocyclic ring –

A compound with atoms from two or more different elements arranged in a ring structure.

At the end of a growing season 20 to 25% of the applied fertiliser N remains in the soil (Stevenson and He 1990). It is gradually incorporated into humic molecules by the process of humification. The mechanisms are not yet understood but may involve the assimilation of fertiliser N into the microbial biomass which is then humified. As the process proceeds the nitrogen becomes increasingly unavailable.

From the 1950s to the 1970s much of the research into commercial humic products focused on the development of nitrogen-enriched coals (NEC) (Berkowitz *et al.* 1970). Also marketed as nitrohumic acids they were produced by oxidising brown coal with nitric acid (Patti *et al.* 1992). In another method, nitrogen fertiliser was mixed with pulverised leonardite, treated with phosphoric acid and called ammonium humate fertiliser (Cooley 1968). Similar products were produced by oxidising biomass waste with nitric acid followed by ammoniation of the oxidised material (Riera *et al.* 1991).

Product claims

Many nitrogen-enriched humic products are still on the market today. In all cases the expectation is that the N-humates will provide a slow-release nitrogen fertiliser to match plant uptake of nitrogen more efficiently than nitrogenous fertilisers (Riera *et al*. 1991). Humic products are also sold as a coating on or mixed with urea with the intention of slowing hydrolysis and the release of nitrogen.

Whilst on the one hand claiming the slow release of nitrogen at a rate commensurable with plant uptake, some manufacturers also market their humic products as having a synergistic effect on nutrient assimilation. This might occur directly due to the improved efficiency of nitrate uptake and indirectly through improved microbial activity, especially those involved with nitrification.

Where's the evidence?

Humates as slow-release nitrogen fertilisers

Initially, reports that the N-humates were equal to or improving plant growth compared with other N fertilisers were positive (Berkowitz *et al*. 1970). However, the nutrient value of the N-humates remained questionable.

Extended field trials in Canada and Australia showed no significant gains (Berkowitz *et al*. 1970). Although initial results from Indian trials were promising, longer-term results were not encouraging. The researchers concluded that there was little available nitrogen in the humates and that any gains in growth might be due to improved soil structure and moisture retention in the fields treated with the humate.

To further test these findings Berkowitz *et al*. (1970) commenced a pot trial with red canary seed. They found an initial improvement in the growth of plants treated with the N-humate but the available nitrogen was quickly exhausted and overall responses were no different from the control. The ensuing N deficiency was reflected in a decrease in plant tissue N with protein being sacrificed for total dry matter.

Improved nitrogen uptake by plants

Berkowitz *et al*. (1970) tested for possible synergism between an N-humate and nitrogen fertiliser. The humate failed to influence plant utilisation of effective N. They concluded that there was no evidence for N-humates functioning as slow release fertilisers or influencing the uptake of available nitrogen in the soil.

Chen and Aviad (1990) reviewed studies into the effects of humic and fulvic acids and Na-humates on the uptake of macronutrients by plants. Several studies showed significant increases in the uptake of nitrogen as well as phosphorus, potassium, calcium, magnesium and sodium. This occurred with a variety of products and range of application rates. Chen and Aviad (1990) suggested that the increase in uptake of macronutrients may be due to the influence of humic products on the rate of nutrient release from the soil.

Piccolo *et al.* (1992) and Pinton *et al.* (1999) also studied the synergistic effects of humic material on nitrogen uptake by plants. Piccolo *et al.* (1992) assessed five humic extracts from oxidised coal, leonardite and an organic soil. They measured nitrate uptake into barley seedlings after incubation for 16 hours with each of the extracts. Nitrate uptake increased with the concentration of the humic extracts to a peak then dropped rapidly at higher concentrations. Maximum uptake occurred at different concentrations depending on the type of extract. The most effective treatment had the highest acid functionality, the lowest molecular weight and was applied at the lowest concentration of 200 µg C/L. It peaked at 29.8% nitrate uptake above the control.

Pinton *et al.* (1999) extracted a humic fraction from sphagnum peat with which they treated germinated maize seedlings at 5 mg organic C/L. The humic extract, in combination with a supply of nitrate ions, increased the uptake of NO_3^- by 70% over the nitrate-only control and modified the development of the seedling roots. The length of the lateral roots increased as did the number of secondary roots. The humic extract led to a similar response when $CaSO_4$ was added rather than nitrate ions.

How does it work?

The concentration of natural humic substances in the soil solution can reach 250 mg/L (Pinton *et al.* 1999). Low molecular weight humic molecules may be able to enter and flow in the apoplast, the space between the cell wall and membrane. In the apoplast they can stimulate H^+-ATPase activity, causing protons to be extruded by the roots which then take up, by cotransport, macronutrients such as nitrogen (Figure 16).

Apoplast –

The space outside a plant's plasma membrane through which water and solutes are transported. This non-living extracellular space includes the cell walls, the spaces between cells and the xylem vessels.

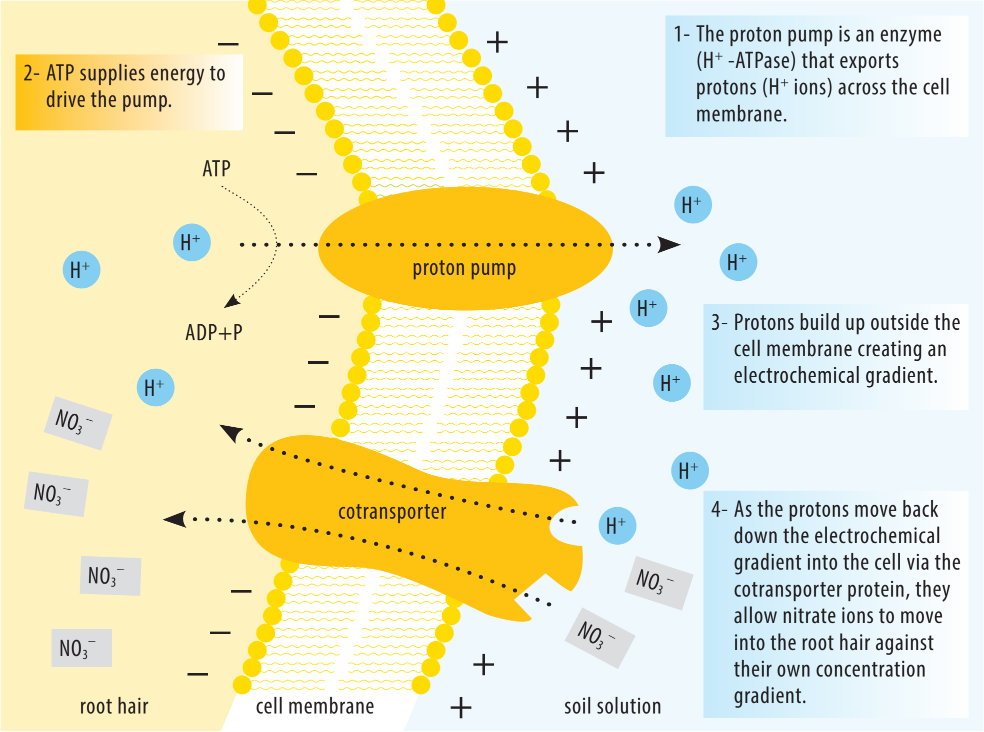


Figure 16 - Proton pumps in the plasma membranes of root hairs enable nitrate ions to be carried into the cells against their concentration gradients. Humic molecules may stimulate this activity.

Proton H^+-ATPase is the enzyme that drives the proton pump in plants allowing the movement of nutrients across root cell membranes and into the xylem. Pinton *et al.* (1999) used enzyme tests to determine the levels of H^+-ATPase in the plasma membrane of the barley roots treated with a humic extract. An increase in activity of 57% was measured for the humic extract with nitrate treatment and a 137% increase occurred with the humic extract on its own.

Improved microbial activity

Krejcová (2010) incubated 30 agricultural soils from across the Czech Republic with 50 g ligno-humate/kg soil. The ligno-humate was extracted from paper mill waste. The addition of the humate shifted the C:N balance in most of the soils in favour of N immobilisation into the microbial biomass. This could potentially extend plant utilisation of N and reduce the risk of leaching but also reduce dry matter production or plant protein.

Khandelwal (1977) assessed the effect of a humate derived from farmyard manure and thiourea on the availability of urea N. Favourable soil pH and temperature conditions led to the complete mineralisation of the urea-only treatment within 15 days. The humate-treated urea had no effect on the rate of N mineralisation whereas the thiourea inhibited *Nitrosomonas* activity, leading to ammonia accumulation in the soil with nitrogen still available after 30 days.

Vallini *et al*. (1997) found that both lignite and compost-derived humic acids increased the growth of *Nitrosomonas europaea* and *Nitrobacter agilis*. The tests were done as culture experiments free from undesirable microorganisms. Microbial cell growth and the oxidation of ammonium and nitrite ions increased with the addition of the humic acids but were independent of the dose rate. Vallini *et al*. (1997) concluded that the bacteria were not using the humic acids as an energy source. They suggested that the humic acids may increase bacterial cell membrane permeability, the absorption of mineral nutrients and energy yielding substrates and thus the growth of the bacteria.

Benedetti *et al.* (1994) expanded previous glasshouse experiments into a field trial with wheat. The pot trial had demonstrated that a peat-derived humic acid mixed with an NPK fertiliser had a positive effect on the metabolism of microorganisms and the N dynamics in the soil. In the field, greater microbial activity was measured in uncropped soil treated with the humic acid relative to the control. However, nitrification, dehydrogenase and urease activities were not modified by the humic treatment in the cropped soils. Competition between the plants and microorganisms for nutrients in the cropped soils was given as a reason for the lack of humic activity.

Potential or presumption?

There is good evidence that, in nitrogen-enriched humic products, the nitrogen is bound so tightly to the humic molecules that it is mostly unavailable to plants. Therefore, these products can not be recommended as alternative N fertilisers. Insufficient studies with humates and urea have been conducted to determine whether humic products have the potential to slow the mineralisation of urea.

There is some laboratory evidence that humic materials may have a synergistic effect on nitrate uptake by plants. Whether commercial humic products can improve N uptake is yet to be tested in pot trials and under field conditions. Also, the ability of such products to affect microbial activity and, hence, nitrogen availability in agricultural conditions is not certain.

A familiar pattern is emerging. Although the published results from laboratory and pot trials are mostly positive, they are not being replicated when extended to field conditions. Until positive and repeatable evidence is available from field trials with Australian crops and pastures it would not be wise to recommend humic products as an amendment to improve nitrogen availability and uptake by plants.

Phosphorus

Background

The amount of organic phosphorus occurring in soils ranges from 15 to 80% of total P depending on the composition and nature of the soil (Stevenson 1994). Organic phosphorus occurs as inositol phosphates, phospholipids and nucleic acids with traces of phosphoproteins and metabolic phosphates. More than half the total P in soils cannot be accounted for in known compounds. It may exist in organic compounds such as phosphate esters bound to humic substances in soils.

Product claims

The claims of humic products relating to phosphorus are similar to those for nitrogen. The humates will complex with P, forming stable phosphates that will be more available to plants. This is somewhat of a furphy as one of the main problems facing Australian agriculture is the formation of far too many stable phosphates that become unavailable to plants over time.

How does it work?

It is this problem of P availability that led researchers to investigate the effects of humic products on alkaline soils with high levels of unavailable calcium phosphates. They were working with the knowledge that humic and fulvic acids will complex with metal ions. In the soil solution, acidic functional groups on the humic molecules dissociate leaving anionic regions with a high affinity for calcium. Competition occurs between the humic acid and phosphate ions for adsorption to the divalent calcium ion (Martinez *et al.* 1984).

Martinez *et al.* (1984) tested the theory in the laboratory, studying the interaction of phosphorite [rock phosphate] with humic acids extracted from a Spanish lignite. Most of the reaction occurred within the first 24 hours with phosphorite solubility, in the presence of humic acid, increasing 4.4-fold at pH 5 and 12.4-fold at pH 7. Lower concentrations of humic acid had a higher capacity to solubilise P. This led to the possibility of adding HA-phosphorite compounds as slow-release fertilisers to calcareous alkaline soils that rapidly bind soluble P fertilisers.

Crystal growth experiments were conducted by Inskeep and Silvertooth (1988). They examined the effect of humic, fulvic, tannic and smaller organic acids on the rate of precipitation of hydroxyapatite (HAP). Fulvic acid was more effective than humic acid at inhibiting HAP precipitation. The lower molecular weight organic acids were not very effective. The fulvic and humic acids competed with phosphate ions in solution for adsorption sites on the HAP seed crystal (Figure 17a).

Where's the evidence?

Lobartini *et al*. (1994; 1998) expanded the laboratory work to pot trials. In their 1994 trial they treated apatite with different rates of humic and fulvic acids extracted from soil. The dissolution of apatite and amount of phosphorus released increased with time, with increasing rates of humic and fulvic acids and with decreasing pH. It was greatest at 800 mg HA/L. The humic acids were more effective than the fulvic acids. Phosphate ions complexed with the humic acids at pH values above neutral and were present as free orthophosphates at pH readings less than 5. Growth of corn in the apatite + HA treatments was significantly greater than the control at pH 5. There was no difference at pH 7.

Lobartini *et al*. (1998) repeated the study to determine the effects of humic and fulvic acids on aluminium and iron phosphates (Figure 17b). Once again, the amount of phosphorus released increased with time and application rate with humic acids having a greater effect than fulvic acids. In a hydroponic trial with maize, humic acids were added to the nutrient solution that had either $FePO_4$ or $AlPO_4$ as the source of phosphorus. The humic acid increased the dry weight and P content of the maize with maximum growth at 400 mg HA/L and iron phosphate as the source of P.

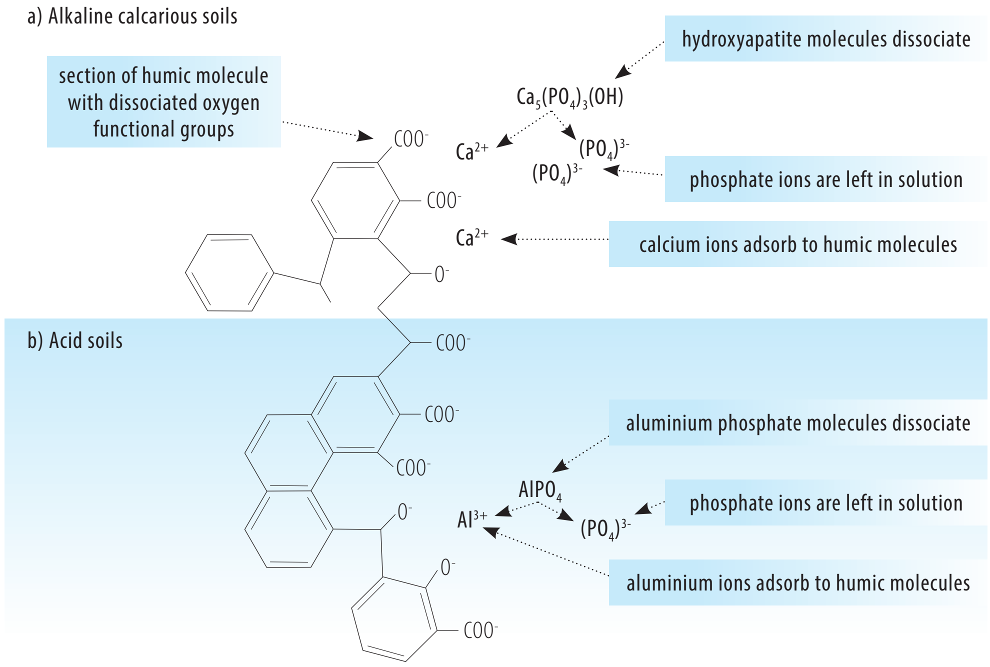


Figure 17 - The effect of humic molecules on phosphorus availability

In another pot trial, Jones *et al*. (2007) assessed the effects of monoammonium phosphate (MAP) coated with commercial humic acids on the growth of spring wheat in both calcareous and non-calcareous soils. The humic acid was applied at the recommended rate of 1.7 kg HA/ha. Although the soluble P concentration rose slightly with the humic treatment by day 4, this was negated by day 8 of the trial. There was no significant effect on shoot biomass, grain yield or the uptake of iron or zinc.

Jones *et al*. (2007) concluded that the label rate was too low to affect the concentration of humic substances already existing in the rhizosphere. Also, the applied humic acid molecules could possibly sorb to other minerals, such as aluminium and iron oxides, to which they have a higher affinity than calcium. However, at adequate concentrations humic acids can compete with phosphorus for adsorption sites to and complexation with Al and Fe ions, acting as powerful chelators of these metals (Lobartini *et al*. 1998). The process of chelation will be discussed in the next section.

The effect of humic materials on plant uptake of phosphorus in laboratory and pot trials has been reviewed by Chen and Aviad (1990). Ryegrass, fescues, maize and vegetables benefited from the addition of either humic or fulvic acids at a range of application rates in terms of P uptake. In another pot trial, Cimrin and Yilmaz (2005) found no effect of humic acids on the head weight of lettuce. The addition of humic acid with phosphorus did, however, increase the uptake of nitrogen. Karr (2001) reviewed three trials in which P uptake was significantly improved by the addition of humic acids. Results from field trials showed both P uptake and yield of wheat increasing by 25% in an alkaline soil to which humic acids had been added along with a phosphorus fertiliser.

Biondi *et al*. (1994) studied the potential leaching of phosphorus from soils treated with humic acid. They conducted field wheat trials with lysimeter tanks on both volcanic and alluvial soils. Soil treated with a humic acid lost 25% more phosphorus than untreated soils. The treated volcanic soil lost 41% P in the leachate and the alluvial soil, 23% P. Biondi *et al*. (1994) suggested two possible mechanisms for this loss of P. The negative charges on the humic acid could be competing for positive sites on the edges of clay particles in the soil, leaving the phosphate ions in solution. Alternatively, as pH decreased and H^+ ions filled the phenolic-OH sites, non-specific adsorption of phosphate ions to the humic molecule could occur. The adsorbed phosphate ions could then move down through the profile with the soluble humic molecules.

Potential or presumption?

There appears to be some evidence that humic products may have a role in improving phosphorus availability in calcareous alkaline soils and also acid soils with high levels of aluminium and/or iron. The role of organic matter, especially humic substances and low molecular weight organic acids, in the complexation of aluminium is well established (Haynes and Mokolobate 2001). Whether additions of humic products can have a significant effect will need to be tested in a variety of soils with varying levels of organic matter and at different pH values.

The use of humic products on soils with high available P analyses should proceed with caution. Soluble P-humate complexes have a greater risk of leaching through the soil profile and could be a problem in terms of phosphorus transport into waterways.

Chelation –

The formation of two or more bonds between a metal ion and another compound, usually an organic molecule.

Ligand –

The organic compound that wraps itself around the metal ion and forms a complex with it.

Metal complexes and chelates

Background

Chelation reactions are essential in soils. A chelate occurs when a metal ion forms two or more bonds with another compound, usually an organic molecule. A number of biochemical compounds, synthesised by microorganisms, extruded by plant roots and found in decomposing litter are capable of chelating metal ions (Stevenson 1994). However, their turnover in the soil is very rapid due to microbial degradation. Humic compounds, on the other hand, are recalcitrant and, by definition have a much longer life span. The formation of metal-HS complexes and chelates are important for:

- The weathering of rocks and minerals;
- Increased availability of phosphate ions;
- Reducing the toxicity of aluminium and heavy metals;
- Forming HS-metal-mineral complexes in soils that improve soil structure;
- Cycling of trace elements in soil; and
- Transportation of trace elements in the rhizosphere to plant roots and microorganisms.

Product claims

The ability of humic molecules to form complexes and chelates with metal ions is well established. This process is vital to plant nutrition and the environment. Humic substances play an important role in both the availability and immobilisation of essential and toxic elements in the soil (Leita *et al*. 1998).

Depending on soil conditions, many trace elements form precipitates and are unavailable to plants. HS-metal chelates are often soluble at pH values that would normally precipitate trace metals (Kaschl and Chen 2005). Conversely, heavy metals may be present in bioavailable forms that are toxic to plants and soil microorganisms. Humic-heavy metal complexes can sorb to mineral surfaces in the soil, immobilising the heavy metals.

Many humic products are sold as natural chelating agents with the promise of improved micronutrient availability to plants. Some are packaged with a complement of trace elements including iron, manganese, copper, zinc, cobalt, boron and molybdenum.

How does it work?

It is the high proportion of functional groups on humic materials that enable them to form metal complexes. All of the groups on humic and fulvic acids, including carboxyls, alcohols, phenols, carbonyls, amines and amides, and sulphates and sulphides, are able to interact with metal species (Spark *et al*. 1997b).

Binding preferences and mechanisms have been described by Stevenson (1994) and Kaschl and Chen (2005). Some metals, such as aluminium and calcium, bind preferentially to the oxygen functional groups. Others, for example zinc, iron, nickel and lead, form stronger complexes with nitrogen and sulphur donor groups. Copper is able to coordinate with all functional groups.

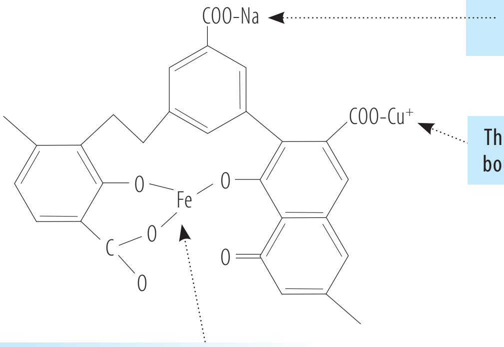
However, it is the oxygen-rich groups, the carboxyls and phenols, which dominate metal complexation due to their large numbers attached to the humic super-structure. The binding capacity of a humic material for a metal is proportional to the content of these groups as measured by total acidity.

Different types of cations complex with humic molecules via different mechanisms and at various strengths (Figure 18). The monovalent cations, Na^+ and K^+ are held with relatively weak ionic bonds to the carboxyl anions ($-COO^-$), forming salts. The multivalent cations form more complex linkages. For example, a copper ion (Cu^{2+}) forms a coordinate complex if it is bound to one anion on the humic molecule:

$$Cu^{2+} + COO^- \rightarrow COO\text{-}Cu^+$$

If the remaining positive charge on the copper ion complexes at another negative site on the humic molecule, a chelate is formed. The copper atom is bound strongly at two points to the humic molecule, which is called the ligand. Two or more linkages form a chelate ring.

The humic molecule acts as a ligand when it forms two or more linkages with a metal ion.



A weak ionic bond forms the salt, sodium carboxlate.

This copper ion forms a coordinate complex bound to one anion on the humic molecule.

Iron forms a chelate ring, strongly bound to three points on the humic molecule.

Figure 18 - The functional groups on humic molecules form different types of complexes with metal ions in the soil solution

The higher the valence of the cation the stronger the potential bonds. Trivalent ions, such as Al^{3+} and Fe^{3+} can bind to three sites on the humic molecule and are held most strongly. Some divalent cations have higher binding strengths than others. A binding series known as the Irving-Williams stability series explains most experimental results:

$Hg > Pb > Cu > Cd \geq Ni \geq Zn > Fe(II) > Ca > Mn$

Metals are bound first at sites that form the strongest complexes. As these sites become saturated the weaker sites that form ionic and hydrogen bonds become more important. The formation of HS-metal complexes is determined by the soil environment, especially pH, electrolyte concentrations and the type of clay minerals present (Spark *et al*. 1997a).

As pH increases, functional groups such as COOH dissociate leaving a net negative charge on the surface of the humic molecule (Kaschl and Chen 2005). From pH 3 to 6, approximately 80% of solid humic acid dissolves resulting in a high proportion of anionic COO^- groups (Spark *et al*. 1997b). The negative charges repel causing the molecule to swell and expose the functional groups to metal ions that may be in the vicinity. As the metals form complexes and chelates, the net negative charge is reduced and the molecule ″collapses″, reducing its solubility (Stevenson 1994).

At low background electrolyte concentrations most metal cations sorb to humic acid at pH levels significantly lower than that needed for the formation of metal hydroxide precipitates (Spark *et al*. 1997b). However, at high electrolyte concentrations copper sorbs at pH 6 to 9 and zinc, cobalt and cadmium will not form complexes in acid conditions (pH<7). The background electrolytes are competing with the metal cations for sites on the humic molecule.

The formation of metal-HS complexes is also dependent on the surface charges of minerals in the soil (Spark *et al*. 1997a). In general, metal binding is lowest in the presence of montmorillonite and highest with kaolinite (Stevenson 1994).

Research into the chemistry of humic-metal chelates is continuing, including practical applications of that work. Most studies have been done with copper and iron and a number with cadmium, zinc and lead (Kaschl and Chen 2005). Research into the effects of humates on mercury, nickel, chromium and cobalt has also been carried out.

Where's the evidence?

Once again the question must be posed – given the quantity of humic substances already in the soil carrying out chelation functions, will the addition of a humic product improve the existing chelation of metals? Many company websites and brochures certainly promote their humic products as capable of either improved availability of trace elements, reduced toxicity of heavy metals, or both.

As with the other properties discussed in this report, all of the scientific research that has established the role of humic substances as metal chelators has been done with extracted or commercial humic materials. Thus, evidence exists that humic products can chelate metals. However, most of the work has been done under controlled laboratory and glasshouse conditions and there is little field evidence.

Micronutrient availability

Kaschl and Chen (2005) summarised results from a series of studies by Chen and others into micronutrient availability. At neutral to slightly alkaline pH values humic acids increased iron availability in melons, improving chlorophyll synthesis and stimulating plant growth. In another trial, ryegrass grown with no iron or zinc had very low chlorophyll levels and retarded growth from the lack of photosynthesis (Kaschl and Chen 2005). Adding humic acids alone led to no improvement in chlorophyll formation. The addition of iron and zinc salts alone resulted in a significant but insufficient improvement. However, when the metal salts were added in the presence of humic acid, chlorophyll synthesis rapidly improved.

Conversely, in a greenhouse study with spring wheat, Jones *et al*. (2007) found no significant difference in the uptake of iron or zinc in the presence of humic acid. They concluded that the recommended application rate of 1.7 kg HA/ha was insufficient to have any effect on metal chelation.

Lobartini and Orioli (1988) treated iron deficient sunflower and *Spirodella* spp. with solutions containing iron chelates in the form of Fe-humate and Fe-EDTA. The absorption of iron from Fe-EDTA was ten times greater than from Fe-humate due to the precipitation of some of the humate with calcium. However, the Fe-humate significantly increased the availability and transport of iron, with a reduction in deficiency symptoms within 72 hours of treatment. The iron was readily transferred by the Fe-humate to the root surface where it was reduced, released from the chelate and transported into the xylem.

Mackowiak *et al*. (2001) also compared humic acids with synthetic chelating agents in a hydroponic experiment growing wheat. There were no significant differences in terms of biomass and seed yield. However, the humic acids did improve iron and zinc availability and prevented early iron deficiency. Given the cost of synthetic chelates, humic acids may provide a cost effective alternative.

It is known that metal chelation is proportional to the concentration of the humic material (Spark *et al*. 1997b). What is not well understood is the fate of the humic-metal chelates in the soil. The complexation of humic acids with metals can be beneficial, or might be deleterious to the soil environment and plants depending on whether certain metals are made more or less available (Ruiz-Haas *et al*. 1998).

Heavy metal availability

When humic molecules interact with metal ions in the soil they can form water-soluble, colloidal or water-insoluble complexes (Kaschl and Chen 2005). If the chelates are soluble the complexed metals will be more available, which is good for trace element availability but not for heavy metals. Conversely, if the chelates bind to soil minerals, heavy metals will be immobilised but so too will trace elements.

In general, the lower molecular weight fulvic acids tend to remain soluble as metal chelates and more mobile in soil (Kretzschmar and Christl 2001). The higher molecular weight humic acids are more strongly sorbed to mineral surfaces, binding chelated metal ions in less available or mobile forms.

Karaca *et al*. (2006) studied the interaction of gyttja and fertilisers on soil parameters in an incubation experiment. The gyttja was an organic/mineral deposit found between the coal layers in Turkish lignite deposits. It was rich in humic acids with an organic matter content of 6 to 40%. Applied at 25 kg/ha, gyttga significantly reduced the availability of cadmium, lead, nickel and zinc.

Bezuglova and Shestapalov (2005) studied Russian soils contaminated with heavy metals, first in incubation studies and then with follow-up field trials. They treated the contaminated soils with brown coals containing 46% humic acids and were able to immobilise zinc and lead to levels below that considered to be toxic. However, the brown coal was applied at 50 t/ha.

Potential or presumption?

Based on this data, it would be tempting to recommend the lower weight fulvic acids as suitable for micronutrient transport and the larger humic acids for the remediation of soils contaminated with heavy metals. There is some evidence that low molecular weight metal-humates can be translocated into the plasma of plants and microorganisms (Perminova and Hatfield 2005). Once again, this is good for growth if the metal is a micronutrient – not so good if it is a toxic heavy metal!

However, there is no agreed standard on the distinction between humic and fulvic acids based on molecular weight (Mayhew 2004b). Also, despite the research carried out to date, there is still not enough information about the fate of humic-metal chelates in soils to make any valid recommendations.

The very nature of humic materials makes this job particularly challenging. The large variability between sources and fractions of humic products is the main limiting factor to their effective use (Perminova and Hatfield 2005). The best equipped laboratories with the latest analytical techniques can not get agreement on the molecular weights of identical humic or fulvic acids (Wolf *et al*. 2001). Therefore, commercial companies will hardly be able to provide their customers with sufficient, cost effective data to make informed decisions.

Remediation of soil contamination

Background

The contamination of agricultural soils has been the subject of several reviews in terms of the sources and types of contamination (Cameron *et al*. 1997; McLaughlin *et al*. 2000), remediation practices (Perminova *et al*. 2005) and the mechanisms involved (Perminova and Hatfield 2005; Stevenson 1994). Pressure to dispose of agricultural, industrial, urban and domestic wastes on land rather than into waterways has increased the risk of contamination (Cameron *et al*. 1997) despite the potential benefits of some biowastes (Gibson *et al*. 2002).

Contaminants include both heavy metals and xenobiotics such as pesticides, dioxins, polycyclic aromatic hydrocarbons [PAHs], polychlorinated biphenyls [PCBs] and the array of petroleum products, oils, paints, solvents and plasticisers common in industrial wastes (Cameron *et al*. 1997).

In September 2002, leading research scientists specialising in humic substances and a group of environmental remediation engineers met in Russia at the NATO Advanced Research Workshop entitled "Use of humates to remediate polluted environments: from theory to practice" (Perminova *et al*. 2005). The working group reviewed the then current status of humic research and remediation technology, identified gaps in the existing knowledge and defined future research needs.

Product claims

Humic substances are seen as potential cost effective materials for *in situ* remediation of contaminated soils due to their recalcitrance and their ability to interact with most chemicals in the environment, especially heavy metals and organochemicals (Perminova and Hatfield 2005). Commercial humate suppliers sometimes promote their products as a buffer against toxic chemicals and heavy metals in the soil.

How does it work?

It is the amphiphilic nature of humic substances that enable them to carry out several different functions. Humic molecules have both polar, hydrophilic parts and non-polar, hydrophobic parts. The polar functional groups, especially carboxyls and phenols, are responsible for ion exchange and complexing/chelating reactions with heavy metals as discussed earlier. The hydrophobic segments of humic molecules are able to interact with organic compounds such as pesticides (Perminova and Hatfield 2005). Extensive studies have shown that humic substances have a high affinity for hydrophobic organic contaminants in soils and sediments (Gunasekara *et al*. 2001).

As with all things related to humic substances, the mechanisms of hydrophobic interaction are not yet fully understood and there are several models that attempt to explain the process. Wershaw (1986) proposed that in the soil solution, humic molecules aggregate into membranes and micelles with hydrophilic exterior surfaces and hydrophobic interiors. Organic compounds partition or move into the hydrophobic interiors in much the same way as fats are caught up in detergent droplets in the washing-up (Figure 19). If the humic molecules sorb to mineral surfaces in the soil the organic contaminants become immobilised (Perminova and Hatfield 2005).

Wershaw's model does not explain all the experimental data. Xing (1998) noted that surface adsorption between hydrophobic surfaces of humic molecules and organic chemicals may contribute to their immobilisation. Stevenson (1994) suggested that more than one mechanism may be involved. This is not just an academic exercise. The binding properties of humic substances need to be characterised so that their function in polluted soils becomes predictable (Perminova *et al*. 2005). Until then their use will be limited.

Where's the evidence?

There is some evidence that the degree of humification of the material may determine its effectiveness in the remediation of either heavy metals or organochemicals (Perminova and Hatfield 2005). Humic substances and products are regularly extracted from the following sources with an increasing level of humification:
Composts < peat < soil < lignite.

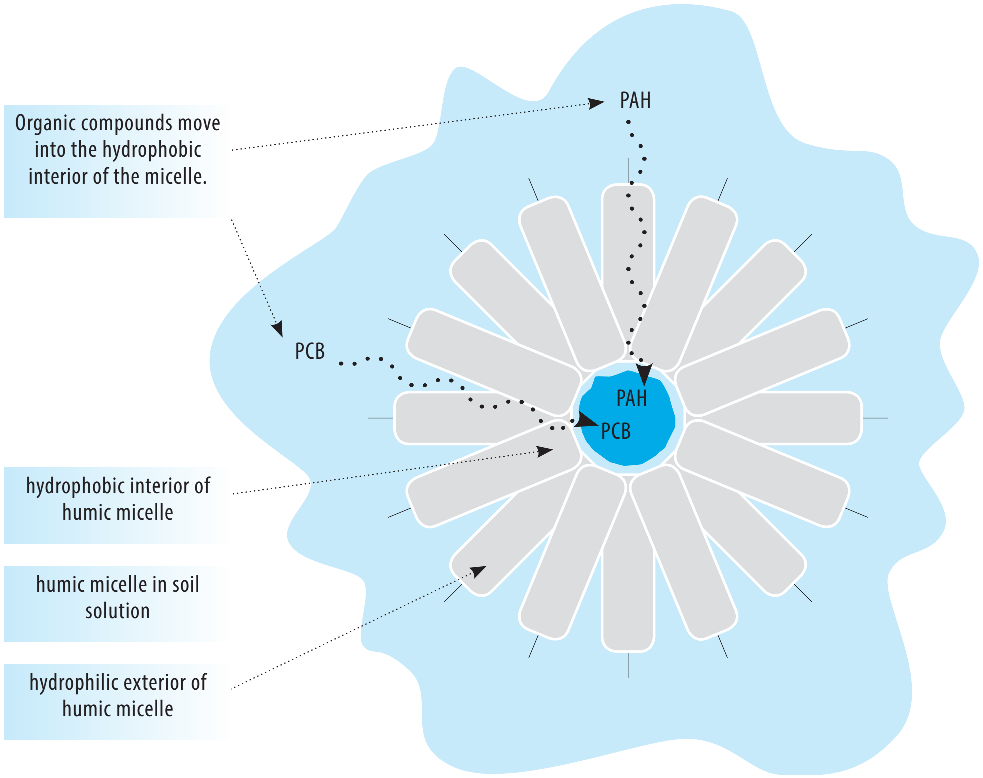


Figure 19 - The immobilisation of organic compounds in humic micelles

As humification proceeds, the percentage of carbon bound in condensed aromatic structures increases and the number of peripheral polar fragments decreases. The more aromatic the structure, the more hydrophobic the molecule and the higher the affinity for organic compounds (Perminova and Hatfield 2005). With a higher percentage of aliphatic polar functional groups there is a greater chance of metal chelation. Therefore, in theory at least, humic products extracted from composts and peats could be more suited to remediation of heavy metal contamination and those from lignites to the immobilisation of organochemicals. This needs to be tested in the laboratory and the field.

The ability of humic substances to complex with organic molecules is also determined by the soil environment, especially soil pH and ionic strength. Increasing pH and ionic strength decrease the affinity of humic acids for PAHs (Diallo *et al*. 2001). The type and source of humic product also has an impact on the final fate of the organochemicals. Lower molecular weight fulvic acids tend to remain soluble, moving complexed organochemicals through the soil profile (Perminova and Hatfield 2005). Larger molecular weight humic acids sorb more readily to mineral surfaces, retaining the chemicals in a less mobile form.

Humic substances are able to carry out a number of other functions that can contribute to the remediation of polluted soils. Among these are redox reactions, where humic molecules donate electrons to or receive them from transitional metals, changing the valence of the metal to a less toxic form. Studies have been undertaken with manganese, iron, mercury, vanadium, chromium and molybdenum (Matthiessen 1994).

Humic substances also have a role in bioremediation. The direct effects of humic products on the physiology of soil microorganisms and plants will be discussed in the next section.

Potential or presumption?

Despite their potential, it is the ability of humic substances to carry out so many functions that is their main limiting factor in soil remediation. There is so much variability between sources and products that their activity in soil cannot be predicted (Perminova and Hatfield 2005). Few natural humic substances have the specific reactive properties needed to fix a particular problem. Their structure needs to be controlled and the humic materials chemically modified to obtain the desired reactivity. To this end, work is progressing on the development of 'designer humics'.

Claims of biological properties

Background

Humic substances have both direct and indirect effects on plant growth. As already discussed, the indirect effects result from improvements in soil physical and chemical properties. There is also a direct physiological influence on plant growth.

In the early 1900s, Bottomley published a series of papers reporting on research into the action of humic substances on a variety of plant species grown in nutrient solutions (Kaschl and Chen 2005). He attributed the enhanced growth to the hormone-like behaviour of humic substances, which he called "auximones". Studies by other researchers in the 1930s including Olsen (Kaschl and Chen 2005) and Burk and others (Clapp *et al*. 2001) suggested that the additional growth may be related to an increased solubilisation and availability of trace metals.

Product claims

Since the 1930s numerous studies have been conducted and a number of other mechanisms proposed, supported by laboratory evidence. Under suitable conditions humic substances have been shown, among other things, to:

- Improve root permeability and ion absorption (Nardi *et al*. 2002);
- Enhance photosynthesis and respiration (Nardi *et al*. 2002);
- Influence enzyme activity (Kulikova *et al*. 2005);
- Generate both free radicals (Paciolla *et al*. 1998) and antioxidants (Kulikova *et al*. 2005); and, even,
- Induce structural changes in the genome of root cells (Durante *et al*. 1994).

Free radical –

Atoms, molecules or ions which are highly chemically reactive due to the presence of unpaired electrons that are available to form chemical bonds

Antioxidant –

A molecule that can inhibit the oxidation of other molecules. Antioxidants are particularly important in blocking chain reactions triggered by free radicals.

Manufacturers of humic products claim a suite of biological properties including those above. Some promote their products as alternatives to plant growth regulators, professing auxin, gibberellin and cytokinin-like activity. There are also claims of improved seed germination, yield and drought resistance, increased chlorophyll biosynthesis, disease resistance and the ability to promote fungal growth, thus overcoming any imbalances in the soil between fungi and bacteria.

How does it work?

For a humic substance, whether commercial or not, to have a direct effect on plant metabolism it must be taken up into the plant tissue. Nardi *et al*. (2002) reviewed studies undertaken with ^{14}C-labelled humic materials. Humic molecules of all molecular weights can be taken up into root tissue. However, the uptake is greater for the lower weight fulvic fractions than for the larger humic acids. Ten to twelve percent of the fulvic acids are transferred into the shoots. This is beneficial to the plant if the fulvic acid is carrying micronutrients. However, if the humic molecule has bound either a heavy metal or toxic organic compound on its way to the plant, the results could be fatal (Perminova and Hatfield 2005).

One of the major controversies relating to the biological properties of humic substances is whether enhanced plant growth is the result of hormone-like properties or enhanced micronutrient uptake. The enhanced activity of microorganisms is also given as an explanation for the apparent hormone-like effects. Microorganisms in the rhizosphere are known to produce auxins and gibberellins (Nardi *et al*. 2002). If humic substances are stimulating microbial populations, their beneficial effects may be accelerated.

Where's the evidence?

The literature is vast, miscellaneous and controversial (Perminova and Hatfield 2005). Each of the above mechanisms is a study in itself and will only be dealt with in general here. Reviews of the literature have been undertaken by Clapp *et al*. (2001), Nardi *et al*. (2002) and Kulikova *et al*. (2005). Different studies into the action of humic substances show different degrees of effect or no effect at all on the particular property being studied (Kaschl and Chen 2005).

There are several reasons for the variability in results. The first relates to the complexity of humic molecular structure and accompanying polyfunctionality – the ability to do a number of things at the same time (Kulikova *et al*. 2005). There is also the issue of the type of humic material used in the investigations. As with the studies of physical and chemical properties, experiments and trials must, by necessity, utilise humic extracts or commercial products. These vary widely in terms of their source, extraction procedures and purification methods (Kaschl and Chen 2005). The third problem facing researchers is that the biological effects of humic substances are more pronounced when the plants are under stress conditions (Kulikova *et al*. 2005). This observation is independent of the type of stress.

To investigate the possible hormone-like effects of humic substances, Chen *et al*. (1994) undertook bioassays of humic extracts from composted manure, composted grape marc [fruit remaining after pressing] and leonardite. They failed to find evidence of plant hormones. Further study demonstrated that increased availability of micronutrients, especially iron and zinc, led to improved plant growth. In a review of the literature, Clapp *et al*. (2001) also concluded that the ability of humic substances to maintain iron and zinc in solution at sufficient levels in the rhizosphere was responsible for growth enhancement.

Nardi *et al*. (2002) also reviewed the literature and came to a different conclusion. They found several examples, both in earlier and more recent literature, which supported the hormone theory. Data was presented demonstrating the extraction of indole acetic acid [IAA] from low molecular weight humic fractions and the inhibition of IAA-oxidase.

In relation to any stimulating effect of humic substances on microbial activity the literature is, once again, not in agreement. Visser (1985) studied the effects of humic and fulvic acids of various molecular weights on different populations of microorganisms. Applications of these humic products, at rates of up to 30 mg/L, increased microbial activity substantially in organic soils, and to a lesser extent in sandy soils. As the molecular weight of the humic fraction decreased the counts went up. At higher concentrations, the applied products were toxic to the microbial populations. Conversely, in a field trial, Mueller and Kussow (2005) found no evidence that humic acids changed the metabolic activity of soil microorganisms.

Potential or presumption?

Companies promoting commercial humic substances are quick to point out the enhancing biological properties of their wares. However, to a large extent, they do this without providing any supporting evidence by way of trial results. It seems that they are relying on those published papers that report positive results, regardless of the circumstances of each particular study. A broader look at the literature continues to reveal contradictory findings. For example, in a review of the action brown coals, Clapp *et al*. (2001) found that some promoted plant growth, whereas others inhibited it.

In all probability, research into the biological properties of humic substances will continue to add more conflicting results to the current body of literature. This is inevitable until the structure of humic substances is understood, the mechanisms of their activity explained and some standardisation of materials and methods employed.

In the meantime, manufacturers and resellers of commercial humics will undoubtedly continue to promote their products, claiming a number of biological properties in an unregulated market.

CONCLUSION AND RECOMMENDATIONS

The companies that manufacture and sell humic products make a number of claims relating to their physical, chemical and biological properties. There is some evidence from laboratory experiments and pot trials that support these claims. However, in 1996, Piccolo *et al*. (Piccolo *et al*. 1996) noted that there was no direct evidence that humic products could ameliorate soils under field conditions. To date, sufficient field trials have still not been conducted to make recommendations to farmers about the efficacy of these products.

Most research is focused on the mode of action of humic substances in soils. The use of humic products, as cheaper alternatives to the extraction of natural humic materials, is adding to the body of literature. There has not been a substantial investment of time and money in repeatable field trials that test the claims of humic products. In an unregulated market, there is no incentive for the manufacturers themselves to make that commitment.

Field trials certainly pose several problems. Soils in general and the rhizosphere in particular are complex systems. Variables that could be controlled in the laboratory and glasshouse are subject to fluctuating environmental conditions in the field. As the coefficient of variation increases, small but possibly significant changes are lost in the noise.

It appears that there may be a role for humic products in agriculture under particular circumstances. The most promising results have come from work related to the availability of phosphorus and micronutrients and the role of humic products in soil remediation. Independent trials are needed to ascertain the conditions and application rates that would benefit plant growth economically.

However, one question keeps repeating itself. If the average Australian agricultural soil already contains 17 t/ha of naturally occurring humic substances, why buy and add any more? Conditions under which humic products would have a reduced benefit have been summarised by Karr (2001):

- Soils with a high organic matter content, especially over 5% SOM;
- Optimum fertility and growing conditions;
- Long-term compost or manure additions;
- Compost additions of more than 5 t/ha in one year;
- Severe limiting factors such as N deficiency, very high or low pH, very wet or cold conditions, soil compaction or plant disease; and
- Application with or after biostimulants such as growth hormones or seaweed extracts.

Karr (2001) also suggested that banding or foliar applications might be more effective than broadcasting humic products and that growers should test a product on a small area of crop before making a large investment.

The other issue is the application rates recommended by manufacturers. Karr (2001) calculated the rate of a humic product required to produce the average increase in plant growth rate as summarised by Chen and Aviad (1990). Assuming that the product has a humic plus fulvic acid content of 70% and allowing for soil interactions and leaching losses, application rates below 100 kg/ha would have little agronomic benefit. The recommended rate for many products is well below this level. Karr (2001) suggested that vendors do this to keep the product at an affordable price whilst gaining an advertising advantage over their competitors and enjoying a large mark-up. Meanwhile, the farmer does not get the purported benefit and researchers have no significant results to report.

Research funding is often scarce. To maximise the value of any funding that may be directed towards humic products the following recommendations are proposed:

- Field trials should focus on those areas of research that have already shown positive results in the laboratory and glasshouse, namely phosphorus and micronutrient availability.
- Trial sites should be chosen to maximise potential results, that is, in soils with reasonable soil structure but low organic matter contents and marginal nutrient levels. Other variables that are likely to compound the results such as soil pH and moisture levels should be controlled.
- Appropriate product analyses should be carried out and compared with the information provided on the label.
- Appropriate soil tests should be conducted before and after the trial.
- A range of application rates should be tested to determine the most efficacious rate regardless of that recommended by the manufacturer.
- The most effective placement or use of the product, for example, seed dressings, banding or foliar use should be investigated.
- A cost-benefit analysis should be conducted at the conclusion of the trial.

Even if field trials provide positive results the retail cost of humic products remains a major limiting factor for their use. In 2010 Gippsland lignites, a popular source for humic products, were selling at US$6.30 per tonne (IER 2010). Although there are capital and operational costs involved in processing raw lignites into humic products, a retail value of $2,500/t seems to provide manufacturers with a substantial margin!

There is a real danger that the situation of the 1970s will be repeated. At that time a combination of "hard sell" marketing and a lack of results in the field turned farmers and agriculturalists away from using humic products and researchers from their study (Kline and Wilson 1994). However, if the work is not done and evidence-based recommendations are not made, sales of humic products will blossom and products will be used in inappropriate situations at ineffective rates. Crop responses will be varied or non-existent and humic products will fade away as yet another alternative fad. The potential of these products will not be realised and in another 30 or 40 years or so, the cycle will repeat itself.

APPENDICES

Appendix 1 – Definitions of humic substances

Some of the most commonly quoted definitions/descriptions of humic substances show the evolution in structural models and resulting terminology. They are:

- Konanova (1966) – Products of advanced decomposition of organic residues and products resynthesised by microorganisms.
- Stevenson (1982) – A series of relatively high molecular weight yellow to black coloured substances formed by secondary synthesis reactions.
- Aiken *et al*. (1985) – A category of naturally occurring, biogenic, heterogeneous organic substances that can generally be characterized as being yellow-to-black in colour, of high molecular weight (MW), and refractory.
- MacCarthy *et al*. (1990b) – A class of organic material resulting from decayed biomatter in soil sediments and natural waters that does not fall into discrete classes of organic substances.
- MacCarthy (2001a) – An enormously complex, amorphous mixture of highly heterogeneous, chemically active yet refractory molecules produced during early diagenesis in the decay of biomatter.

Appendix 2 – References used for Tables 2 – 4

Data from these references was analysed to compile the mean elemental composition of humic acids (Table 2) and fulvic acids (Table 3) and the mean acidic functional group analysis of both humic and fulvic acids (Table 4).

Reference	Tables 2 & 3 Elemental composition	Table 4 Total acidity
Anderson *et al*. (2001)	✓	
Ayuso *et al*. (1996)	✓	✓
Inskeep and Silvertooth (1988)	✓	✓
Kretzschmar and Christl (2001)	✓	
Lobartini *et al*. (1992)	✓	✓
Malcolm and MacCarthy (1986)	✓	✓
Mayhew (2004b)	✓	
Piccolo *et al*. (1992)	✓	✓
Qiang *et al*. (1993)	✓	✓
Rice and MacCarthy (1991)	✓	
Schnitzer *et al*. (2001)	✓	✓
Selim *et al*. (2009)	✓	
Shinozuka *et al*. (2001)		✓
Stevenson (1994)		✓
Tan *et al*.(1992)	✓	✓
Valdrighi *et al*.(1996)	✓	
Varshovi and Sartain (1993)	✓	✓

Appendix 3 – Companies and websites used in the survey of humic products

The following websites were current at the time of writing.

Advanced Nutrients: www.advancednutrients.com.au

Agrichem: www.agrichem.com.au

AustFor Pty Ltd: www.austfor.com.au

Bio-Tech Organics: www.biotechorganics.com.au

GroundGrocer.com Earth Supplies: www.groundgrocer.com

Monty's Plant Food: www.montysplantfood.com

Neutrog Fertilisers: www.neutrog.com.au

Nutri-Tech Solutions (NTS): www.nutri-tech.com.au

Omnia Specialties Australia Pty Ltd: www.australianhumates.com

Seasol: www.seasol.com.au

Soil Solutions Aust. Pty Ltd: www.soilsolutions.com.au

SprayGro Liquid Fertilisers: www.spraygro.com.au

TNN Industries: http://tnn.com.au/

Ultimate Products (Aust): www.ultimateagri.com.au

Ylad Living Soils: www.yladlivingsoils.com.au

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GLOSSARY

Acid: A substance which donates protons into solution and reacts with a base. Acid solutions have a pH of less than 7.

Adsorption: The adhesion (sticking) of atoms, ions or molecules to a surface.

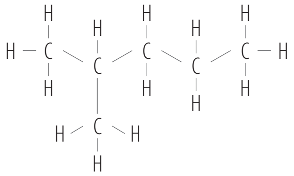
Adsorption strength: The strength with which cations are held onto clay and humic colloids in soil. The adsorption strength of a cation increases with its electrical charge and decreases with its size. For example, Al^{3+} is adsorbed more strongly than Ca^{2+} due to its higher positive charge. Ca^{2+}, in turn, is held more strongly than Mg^{2+}. Magnesium is a larger ion than calcium. The H^+ ion is very small but has a high charge density. Therefore it uniquely sits between Al^{3+} and Ca^{2+} in the series of cation adsorption strengths:

$Al^{3+} > H^+ > Ca^{2+} > Mg^{2+} > K^+ = NH^{4+} > Na^+$

Aguja: An organic-mineral soil found in the Big Bend region of Texas, USA.

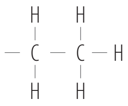
Alcohol: An organic compound with a hydroxyl functional group (OH) bound to a carbon atom. Ethanol (C_2H_5OH) is the most commonly used alcohol as a car fuel, an industrial solvent and in alcoholic beverages.

Aliphatic: Organic compounds with the carbon atoms arranged in straight or branched chains, or non-aromatic saturated rings, where all the available bonds to the carbon atoms are occupied. In organic chemistry, aliphatic and aromatic are opposites, that is, an aliphatic compound can also be called a non-aromatic compound.

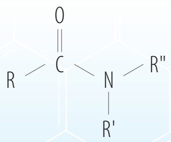


Alkaline: A solution with a pH value greater than 7.

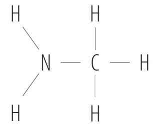
Alkyl group: A functional group or side-chain made up only of single bonded carbon and hydrogen atoms, attached to a larger hydrocarbon molecule. Alkyls are usually abbreviated with the symbol 'R'.



Amide: An organic compound with a carbonyl group attached to a nitrogen atom. Amides are commonly formed when a carboxyl group on one molecule reacts with an amino group from another molecule, creating an amide (peptide) bond. The amide bond gives molecules structural rigidity.



Amine: Organic compounds derived from ammonia with one or more hydrogen atoms replaced with a hydrocarbon group. Amines are found everywhere in nature, in amino acids, proteins, hormones and neurotransmitters. They are basic compounds with a 'fishy' odour.



Amino acid: Organic molecules containing an amine (-NH_2) group, a carboxylic acid (-COOH) group and a side chain specific to each amino acid. There are 20 amino acids that are the building blocks of proteins where they are linked in chains by peptide bonds.

Ammoniation: Treatment with ammonia.

Amphiphile: A molecule with both hydrophilic (water-loving) and hydrophobic (water-fearing) parts. One end of the molecule is attracted to water and the other end to non-polar solvents such as oils. Detergents and cell membranes are composed of amphiphiles.

Anion: A negatively charged ion.

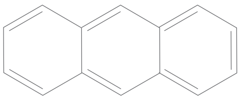
Antioxidant: A molecule that can inhibit the oxidation of other molecules. Antioxidants are particularly important in blocking chain reactions triggered by free radicals.

Apatite: A group of related calcium phosphate minerals commonly referred to as hydroxyapatite (hydroxyl apatite), fluorapatite, chlorapatite and bromapatite depending on the relative concentrations in the crystal of OH^-, F^-, Cl^- and Br^- ions respectively. Apatite (calcium phosphate) is the most common phosphate mineral and is a key part of the phosphorus cycle in soils where it is the main source of P for plant uptake. It is also the major component of teeth and bones in vertebrates.

Apocrenic acid: An early name for humic acid, first extracted by Hermann in 1841.

Apoplast: The space outside a plant's plasma membrane through which water and solutes are transported. This non-living extracellular space includes the cell walls, the spaces between cells and the xylem vessels.

Aromatic: An organic compound based on the benzene ring. Aromatic molecules are more chemically stable than similar non-aromatic molecules because the electrons are shared between all the carbon atoms in the ring. Anthracene, found in coal tar, is a simple aromatic molecule comprising three fused benzene rings.



Anthracene

ATP/ADP: Adenosine triphosphate (ATP) and adenosine diphosphate (ADP) are coenzymes that transport chemical energy within cells enabling chemical reactions to take place.

$ATP + H_2O \rightarrow ADP + P + energy$
$ADP + P + energy \rightarrow ATP + H_2O$

Auximone: Any growth-promoting substance that principally occurs in sphagnum peat decomposed by nitrogen bacteria. The term 'auximone' was coined by Bottomly in 1915.

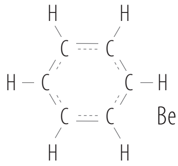
Auxins: A class of plant hormones that promote and regulate growth and development. Auxins are produced in the meristems, or growing tips, of shoots and roots. They increase the plasticity of cell walls allowing the cells to expand and elongate. Auxins are also involved in cell division and differentiation, flowering and fruiting and the inhibition of lateral buds.

Average age: A measure of the age of organic matter in soils – the average time that all of the carbon atoms currently in the reservoir will spend there.

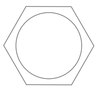
Banding: A practice where fertiliser is placed in a band either on top of or under the soil surface, close to but not in contact with sown seed.

Basic cations (Bases): Cations formed from elements in Group 1, the alkali metals, and Group 2, the alkaline earth metals from the periodic table. These metals all react with water to form strong alkaline (basic) hydroxides. The four basic cations of importance in soil are Na^+, K^+, Mg^{2+} and Ca^{2+}.

Benzene: An aromatic hydrocarbon with an unsaturated ring structure and the molecular formula C_6H_6. The arrangement and sharing of electrons around the ring make benzene and its derivatives very stable molecules.



Benzene – molecular structure



Benzene – aromatic layout

Bioassay: A scientific procedure in which the concentration, purity and/or biological activity of a substance is determined by its effect on living tissue.

Biogenic: Produced by or arising from living things.

Biomass: The total mass of living matter in a given area.

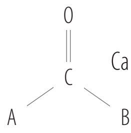
Black carbon: Soot or char resulting from the incomplete combustion of organic matter.

Bond energy: A measure of the strength of a chemical bond between atoms or ions in a compound. The higher the bond energy, the harder it is to break the bond and the more stable the compound.

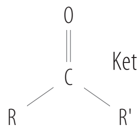
Bridge: In chemistry – an atom, a covalent bond or an unbranched chain of atoms that connect two ends of a ring or loop in a compound.

Carbon sequestration: The removal of carbon dioxide from the atmosphere to deposit it in a reservoir for long-term storage.

Carbonyl group: A family of chemical functional groups with an oxygen atom connected to a carbon atom by a double bond. Depending on where the oxygen-bound carbon atom sits in the chain and the presence and location of other functional groups, a number of different types of organic compounds can result such as carboxylic acids, ketones and amides.

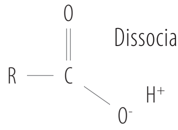


Carbonyl group



Ketone

Carboxyl group: A functional group with the formula –C(=O)OH, usually written as –COOH. A carboxyl contains both a carbonyl (=O) and a hydroxyl (OH) attached to the carbon atom. The hydrogen ion (H^+) can dissociate from the remainder of the functional group ($–COO^-$) giving carboxyls an acidic nature.



Dissociated carboxylic acid

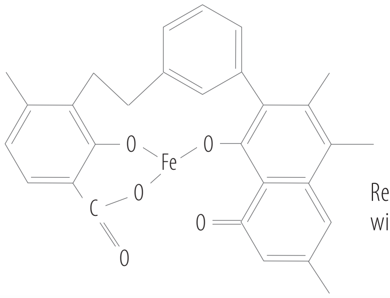
Catalyst: A substance which starts, speeds up or slows down a chemical reaction between other atoms or molecules. Catalysts are not consumed by the reaction. If they are changed during the reaction they return to their original form when it is completed.

Cation: A positively charged ion.

Cation exchange capacity (CEC): The maximum quantity of total cations that a soil is capable of holding at a particular pH value. The cations are held by electrical attraction to the negative charges on clay and humic colloids in the soil and released into the soil solution in response to the concentration of each cation in that solution.

Cellulose: A polysaccharide consisting of a linear chain of several hundred to more than 10,000 glucose molecules. Cellulose is a structural component of plant cell walls and is the most common organic compound on Earth.

Chelation: The formation of two or more bonds between a metal ion and another compound, usually an organic molecule. The organic molecule, called the ligand, wraps around the metal ion like the claws of lobster.



Representation of an iron chelate complex formed with a portion of a humic molecule

Chitin: A long chain organic polymer derived from glucose found in the cell walls of fungi and the exoskeletons of insects and crustaceans.

Colloid: Microscopic particles dispersed evenly through another medium.

Cometabolism: The degradation of two compounds at the same time by enzymes produced by a microorganism. The first compound serves as an energy source while the second compound, which is not used for growth by the microorganism, is also transformed. Cometabolism is used for the biological degradation of hazardous substances.

Complexation: The ability to form coordinate or metal complexes.

Coordination complex: An atom or cation bonded to an arrangement of molecules or anions that surround it.

Cotransport: The simultaneous transfer of molecules or ions across a biological membrane. One of the species moves down its own concentration gradient carrying the other species from an area of low concentration to an area of high concentration.

Cuticle: The tough, flexible outer covering of an organism.

Cutin: A waxy polymer that is the main structural component of plant cuticles, the protective outer covering of leaves and stems.

Cytokinin: A class of plant hormones that promote cell division in shoots and roots. As well as affecting cell growth and differentiation, cytokinins also influence apical dominance, that is, the growth of the central stem. They are also involved in lateral growth and leaf senescence.

Dalton: A unit of measure for the mass of an atom or molecule. Also known as the unified atomic mass unit (amu), one Dalton is defined as one twelfth of the mass of a carbon-12 atom. Named after John Dalton who developed modern atomic theory, a Dalton is approximately equal to the mass of one proton or one neutron.

Dehydrogenase: An enzyme that oxidises a substrate by transferring hydride (H-) ions to a third species that accepts the hydride ions in an oxidation-reduction reaction.

Diagenesis: The physical, chemical and biological changes that occur in deposited sediments as they become consolidated into rocks. These changes occur at relatively low temperatures and pressures.

Dioxins: A group of toxic organic compounds that persist in the environment for a long period of time. They are formed as by-products of combustion and a number of industrial processes. Dioxins can accumulate in the body fat of animals, including humans, and increase the risk of cancer.

Dispersion: The separation of particles in another medium. Soil dispersion occurs when clay particles separate from each other in a wet soil. In sodic (high sodium) soils the sodium ions (Na^+) attach to the surface of clay particles, forcing them apart. A cloud of clay forms around the soil aggregate containing the dispersed, fine clay particles that can clog up micropores and restrict water and air movement and plant growth.

Dissociation: The chemical process in which ionic compounds separate into ions or radicals.

Divalent: An ion with a valence, or net electric charge, of two allowing it to form two bonds with other atoms, ions or molecules. Calcium (Ca^{2+}) and magnesium (Mg^{2+}) form divalent cations and the sulphate ion (SO_4^{2-}) is a divalent anion.

EDTA: Ethylenediaminetetraacetic acid (EDTA) is a colourless water-soluble solid that is used as a ligand to chelate metal ions such as calcium (Ca^{2+}) and iron (Fe^{3+}). It has many industrial uses as well as softening water and making iron more available in calcareous soils.

Electric dipole: A separation of positive and negative charges in an atom or molecule.

Electrochemical gradient: A difference in the electrical potential (electric charge) and chemical concentration across a membrane. For example, when protons (H^+) build up on the outside of a cell membrane due to the activity of the proton pump, the solution on the outside becomes more acidic and more positively charged than that on the inside. This gradient allows cations to enter the cell.

Electron diffraction: An analytical technique in which a beam of electrons is fired at a sample placed in an electron microscope and the resulting interference pattern is observed and measured. Electron diffraction is used to study the structure of crystalline and non-crystalline, or amorphous, solids.

Electron microscope: A microscope that uses a beam of electrons to illuminate particles which are too small to be seen with a light microscope. Because electrons have such a short wavelength, electron microscopes can produce a clear image at magnifications up to 10 million times.

Electron spin resonance (ESR) spectrometry: An analytical technique that measures the radiation absorbed by the electrons of a sample placed in a strong magnetic field. ESR spectrometry has many applications in chemistry and biology, especially the study of free radicals and transition metal ions.

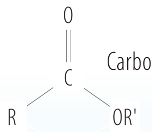
Electrostatic interactions: Forces functioning inside macromolecules that maintain and stabilise the molecular structure. Large molecules can develop areas of electric charge from ionised side chains, such as amino acids, and dipoles, for example, peptides. These positive and negative polar areas develop electrostatic fields and interact with each other, causing the molecule to fold and wrap into a particular structure.

Empirical formula: The simplest ratio of atoms of each element present in a chemical compound, expressed in positive integers (whole numbers). Empirical formulas take no account of the structure or arrangement of a compound or the actual number of atoms. For example, the molecular formula for glucose is $C_6H_{12}O_6$ but its empirical formula is CH_2O, which it shares with acetic acid (molecular formula CH_3COOH) and formaldehyde (CH_2O).

Emulsify: To disperse one liquid into a second liquid into which it would normally not mix.

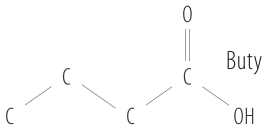
Enzyme: A protein that catalyses (starts or changes the rate of) a chemical reaction in biological systems.

Ester: A chemical compound formed by condensing an acid with an alcohol. Esters occur naturally in fats and oils and are used in fragrances.



Carboxylic acid ester

Fatty acid: A carboxylic acid with a long, unbranched aliphatic tail or chain. Saturated fatty acids have no double bonds in the carbon chain. Those with one or more double bonds are known as unsaturated fatty acids.



Butyric acid, a short-chain fatty acid

Field capacity: A measure of the water holding capacity of a soil. Field capacity is usually measured as the amount of water remaining in a soil after it has been saturated and allowed to drain for up to 48 hours.

Fertigation: The application of water-soluble products, such as fertilisers or soil amendments through an irrigation system.

Flocculate: To aggregate particles dispersed in a colloid into larger clusters called floc or flakes.

Flux: The rate of flow of molecules across a certain area.

Foliar: Of or relating to leaves.

Fractionation: A separating process in which a mixture is divided up into a number of smaller fractions according to a gradient. For example, in a fractionation or distillation column a liquid mixture is separated depending on the boiling points of each fraction. In column chromatography the different fractions move through the column at different speeds.

Free radical: Atoms, molecules or ions which are highly chemically reactive due to the presence of unpaired electrons that are available to form chemical bonds.

Fulvate: A salt of fulvic acid, such as potassium or calcium fulvate.

Fulvic acid: The fraction of humic substances soluble in water under all pH conditions.

Genome: All of the hereditary information of an organism encoded as DNA and/or RNA.

Gibberellin: A class of plant hormones that control stem elongation by stimulating cell elongation and division. Gibberellins also influence enzyme production, germination, dormancy, flowering and leaf and fruit senescence.

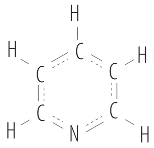
Gyttja: A Swedish word for the fine-grained mud that accumulates at the bottom of freshwater lakes, ponds and bogs. Gyttja contains large amounts of organic material.

H^+-ATPase: The enzyme that drives proton pumps in plants, also called proton-ATPase. Oxidation reactions occurring across the cell membrane move protons (H^+) to the outside of the cell. As the protons build up an electrochemical gradient is produced. The solution on the outside of the membrane is more electrically positive and more acidic than that on the inside of the cell. This gradient allows solutes to enter the cell, often attached to carrier proteins.

Heavy metals: A general term for a group of elements that have metallic properties, most with relatively high atomic weights. Some, such as iron, copper and molybdenum, are essential micronutrients for plants and/or animals but can be toxic in large doses. Other heavy metals, for example mercury and lead, have no known benefits to organisms and accumulation in their tissues can have serious consequences.

Hemicellulose: A polysaccharide made up of two or more single sugars such as glucose, xylose and mannose arranged in branching chains. Hemicellulose has a random, amorphous structure and is found in most plant cell walls.

Heterocyclic ring: A compound with atoms from two or more different elements arranged in a ring structure. Most heterocyclic compounds are organic, containing one or more carbon atoms and another element, such as sulphur, oxygen or nitrogen in the ring.



Pyridine – a heterocyclic compound

Heterogeneous: Made up of different parts.

Heterotrophy: The consumption of organic molecules by an organism to use as an energy source. Heterotrophs cannot use sunlight or inorganic compounds as a direct source of energy.

Hulis: Humic-like substances found in the atmosphere and extracted from aerosol particles and water droplets in fogs and clouds.

Humate: A salt of humic acid, such as potassium or calcium humate.

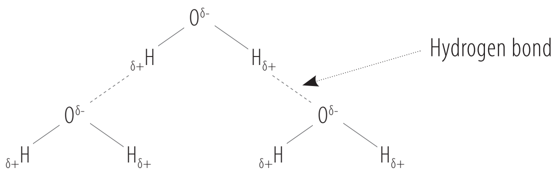
Humic acid: The fraction of humic substances not soluble in water at pH values lower than 2 but soluble at higher pH values.

Humification: The chemical and microbiological processes that transform the dead remains of living things into humic substances.

Humin: The fraction of humic substances not soluble in water at any pH value.

Humus coal: An early name for humin, first extracted from humus and named by Sprengel in 1826.

Hydrogen bond: A relatively strong type of bond that occurs between molecules or different chemical groups attached to the same molecule. Hydrogen bonds form when hydrogen atoms with a net positive charge (δ+) on one molecule are attracted to electronegative (δ-) atoms on the other molecule such as nitrogen, oxygen or chlorine atoms. The high boiling point of water is due to the formation of hydrogen bonds between water molecules.



Hydrolysis: chemical reaction during which water molecules (H_2O) are split into hydrogen cations, or protons (H^+) and hydroxide anions (OH^-).

$H_2O \rightarrow H^+ + OH^-$

Hydrophilic: A molecule or part of a molecule that is attracted to and can be dissolved in water (literally – 'water loving' or 'water friend'). Electric charges in hydrophilic molecules tend to polarise so that one end has a net positive charge and the other a net negative charge.

Hydrophobic: A molecule or part of a molecule that is repelled by water (literally – 'fear of water'). Hydrophobic molecules tend to be non-polar with no areas of net electric charge. When placed in water they often cluster together in micelles or droplets. Hydrophobic molecules can dissolve in non-polar solvents such as oils.

Hydrophobic forces/interactions: The tendency of hydrophobic organic molecules to form aggregates in an aqueous medium, for example, oil forming droplets on water. As the individual hydrophobic molecules repel water they tend to clump together. The surrounding water molecules attract each other and squeeze the hydrophobic molecules into larger aggregates.

Hydroponics: A method of growing plants in water containing essential mineral solutions but without soil.

Hydroxyapatite (Hydroxylapatite): A naturally occurring mineral form of apatite (calcium phosphate) with a high concentration of hydroxyl ions and the formula $Ca_5(PO_4)_3$ (OH).

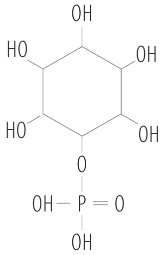
Hymatomelanic acid: An early name for humic acid, first extracted by Hoppe-Seyler in 1889.

IAA-oxidase: The enzyme that breaks down IAA, thus controlling the level of IAA in plants and having an indirect effect on plant growth.

Indole-3-acetic acid (IAA): The first auxin to be isolated in the 1930s. IAA is produced by the growing tips of plants and induces cell elongation and division. A number of synthetic IAA derivatives have been produced that are used variously for vegetative propagation, plant tissue culture and as herbicides.

Infrared spectrometry: A spectrometry technique that measures how a sample absorbs and reflects infrared wavelengths of light. It is has a wide range of applications including providing information about the structure, purity and identification of an organic compound.

Inositol phosphate: An organic form of phosphorus comprising a cyclic molecule with hydroxyl groups and one or more phosphate groups attached. Inositol phosphates are crucial in several cellular functions including cell growth and differentiation and programmed cell death.



Inositol monophosphate

In situ: A Latin phrase which literally means 'in its original position or place'. *In situ* studies involving soils are done in the field.

Ionisation: The physical process in which atoms or molecules are converted into electrically charged ions. A positive ion, or cation, is produced when an atom loses one or more electrons, leaving a net positive charge. An anion is formed when one or more free electrons collide with an atom, producing a net negative charge.

Isotope: Atoms of a particular element that have differing numbers of neutrons. For example, all carbon atoms have 6 protons but can have 6, 7 or 8 neutrons, resulting in the isotopes carbon-12 (^{12}C), carbon-13 (^{13}C) and carbon-14 (^{14}C) respectively.

Kaolinite: A soft, white clay found in soils, produced by the chemical weathering of feldspar and other minerals high in aluminium silicate minerals. Kaolinite is the most important 1:1 clay made up of layers of one silicate sheet and one alumina sheet. It has a low shrink-swell capacity and a low CEC, having a relatively low content of bases.

Labile (active) pool: Organic matter in the soil that can undergo microbial breakdown, releasing nutrients for plant growth.

Leaching: In agriculture, the loss of water-soluble nutrients carried down through the soil profile by percolating water.

Leonardite: A form of lignite that is rich in humic acid. Leonardites have a soft waxy, shiny, black or brown appearance.

Ligand: An ion, molecule or a functional group on a macromolecule that binds to a central metal atom forming a coordination complex or chelate with multiple bonds between the metal and the ligand.

Ligand exchange: A chemical reaction in which one ligand in a coordination complex is replaced by another ligand.

Light fraction: Plant residues in varying stages of decomposition that exist within the soil.

Lignin: A complex organic compound most commonly found in wood. Lignin is highly aromatic and more resistant to microbial degradation than less complex molecules such as cellulose.

Lignite: Brown coal – sedimentary rocks formed from layers of decomposing vegetation with a carbon content of 25% to 35%, a high moisture content (up to 66%) and an ash content of 6% to 19%.

Ligno-humate: A humic product derived from wood or other organic material containing lignin.

Lipids: A group of hydrophobic or amphiphilic organic molecules which includes fats, oils, waxes, sterols and fat-soluble vitamins.

Lipoprotein: An organic molecule containing both lipids and proteins within its structure.

Litter: Plant and animal residues that lie on the soil surface.

Lysimeter tank: A device used in the field to measure drainage through soils and any substances dissolved in the percolating water.

Macromolecule: A very large molecule usually formed by the process of polymerisation where smaller molecules combine chemically to form three-dimensional networks or polymer chains.

Macronutrients: Elements required in relatively large amounts by organisms. The macronutrients essential for plant growth are carbon, oxygen, hydrogen, nitrogen, phosphorus, potassium, sulphur, magnesium and calcium.

Marc: The solid remains of fruit, such as grapes or olives, after it has been pressed for juice or oil. Also known as pomace, marc contains the skins, pulp, seeds and stems of the fruit.

Marl: Fine-grained sedimentary clays and chalks. Marl is often a soft, moist, unconsolidated deposit of calcium carbonate (limestone) mixed with earth.

Mean (average) residence time: A measure of the age of organic matter in soils – the average time an individual carbon atom has spent in the reservoir at the point when it leaves.

Melanin: An organic pigment found in most organisms where it has a role in protection against a number of potential stresses such as ultraviolet radiation, high temperatures, heavy metals and invading microbes.

Metabolic phosphates: Phosphate molecules that store or give off energy in cells. Examples are adenosine triphosphate (ATP) and adenosine diphosphate (ADP), coenzymes that transport chemical energy within cells enabling chemical reactions to take place.

$ATP + H_2O \rightarrow ADP + P + energy$
$ADP + P + energy \rightarrow ATP + H_2O$

Micelle: An aggregate or cluster of surfactant molecules suspended in a liquid. Typically, the molecules are aligned so that their hydrophobic (water-hating) tails are buried in the centre of the micelle with the hydrophilic (water-loving) heads facing out into, and adsorbing onto the liquid molecules, thus lowering the surface tension. Micelles are often spherical in shape.

Microbial biomass: The total mass of microorganisms living in a particular volume of soil.

Micronutrients: Elements required in relatively small amounts by organisms. Also known as trace elements, the micronutrients essential for plant growth are copper, zinc, manganese, boron, molybdenum, cobalt and iron.

Micropore: Soil pores that are less than 2 nanometres (nm) in diameter. The water held in micropores is unavailable to plants as it is usually adsorbed to clay surfaces but it is important for microorganisms and soil chemical reactions.

Monovalent: Ions with only one valence bond.

Montmorillonite: A very soft, white to brownish yellow clay found in soils, also called bentonite or smectite. Montmorillonite is a 2:1 clay made up of layers of one alumina sheet sandwiched between two silica sheets. This clay swells as it absorbs water then shrinks as it dries out. Montmorillonites have a relatively high content of bases and a high CEC.

N immobilisation: The conversion of inorganic nitrogen (NH_4^+ and NO_3^-) to organic forms by microorganisms.

Nitre: Potassium or sodium nitrates.

Nitric acid: A highly corrosive, toxic mineral acid with the formula HNO_3.

Nitrification: The biological oxidation in soils of ammonium (NH_4^+) to nitrate (NO_3^-) ions. Nitrification is a two-step process with the ammonium ions first being oxidised to nitrite (NO_2^-) mainly by *Nitrosomonas* bacteria. Then the nitrite is further oxidised to nitrate chiefly by the genus *Nitrobacter*.

Nitrobacter agilis: One of the species of the *Nitrobacter* genus of bacteria that oxidise nitrite (NO_2^-) to nitrate (NO_3^-) in soils. *Nitrobacter* gain their energy from the oxidation process and do not need a source of carbon.

Nitrohumic acid: A humic product produced by oxidising brown coal with nitric acid.

Nitrosomonas europaea: The bacterium most responsible for the oxidation of the ammonium ion (NH_4^+) to nitrite (NO_2^-) in soils. *N. europaea* does not need a source of carbon for energy. Instead it gains its energy from the oxidation of ammonia.

Non-humic fraction: Discrete organic compounds in soils that can be purified and have a definite molecular structure such as sugars, polysaccharides, amino acids and proteins.

Nuclear magnetic resonance (NMR): An analytical technique with many applications including determining the molecular composition and structure of a sample. The nuclei of different atoms absorb and emit unique frequencies of radiation. When a sample is placed in a strong magnetic field the frequencies of the absorbed and emitted radiation are measured and help to build a picture of the molecules in the sample.

Nucleic acids: Biological macromolecules that make up the genetic material of life, deoxyribonucleic acid (DNA) and ribonucleic acid (RNA).

Organic acid: An organic compound with acidic properties. Examples of organic acids are the carboxylic acids (R-COOH) such as formic acid that gives ants their strong odour (HCOOH) and acetic acid or vinegar (CH_3COOH).

Organo-clay complex: Organic molecules chemically bonded to clay minerals. Organo-clay complexes make up the primary structure of soils.

Orthophosphate: The simplest in a series of phosphate ions with the formula PO_4^{3-}. Orthophosphate is often called phosphate.

Oxidation: The net loss of electrons from a molecule, atom or ion. Originally, oxidation referred to the addition of oxygen to a compound and reduction to the removal of oxygen. As similar reactions were studied the definition was gradually widened and explained by the transfer of electrons in, what are now known as, redox reactions.

Partition: The movement of a molecule between two solvents that will not mix.

Passive (stable) pool: The humic fraction of soil that resists microbial breakdown.

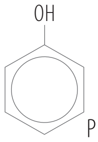
Pathogen: An organism or agent that causes disease.

Peptide: Short chains of amino acids connected by peptide bonds.

Permanent wilting point: The moisture content of a soil at which plant roots can no longer extract water. The plant wilts and can not recover.

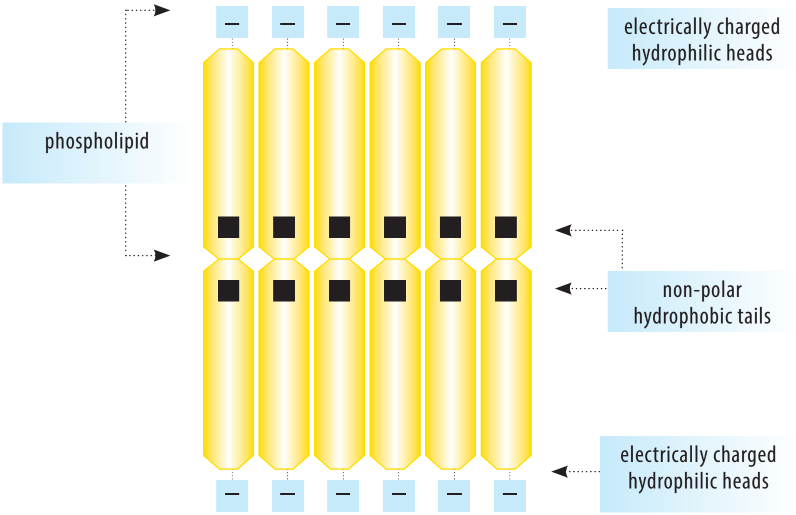
pH: A measure of acidity or alkalinity. The pH scale ranges from 0 to 14 and is measured as the negative logarithm of the concentration of hydrogen ions in a particular solution. At a pH of 7 the solution is neutral. Below 7 the solution becomes more acid and above pH 7 the solution becomes more alkaline or basic.

Phenol: Also known as carbolic acid, phenol is an organic compound based on the benzene ring with the chemical formula C_6H_5OH. Hydrogen ions dissociate from the hydroxyl (-OH) groups giving phenol its mildly acidic nature.



Phenol

Phospholipids: A class of lipids that are a major component of cell membranes where they form lipid bilayers, two very thin layers of lipid molecules. Phospholipids have a hydrophilic head and a hydrophobic tail. In the cell membrane the hydrophilic heads face out and the hydrophobic tails all point in towards the centre of the two layers.



Phospholipids in a cell membrane bilayer

Phosphoprotein: Any group of proteins that are chemically bound to phosphoric acid. An example is casein, a phosphoprotein found in milk.

Phosphoric acid: A group of mineral acids with the basic chemical formula H_3PO4.

Phosphorite: A sedimentary rock that contains at least 15% to 20% of phosphate bearing minerals. Also called rock phosphate, phosphorite is derived from a number of sources including marine invertebrates with shells composed of calcium phosphate and the bones and excrement of vertebrates. Islands of guano, the faeces and urine of seabirds, seals and cave-dwelling bats, have been mined for hundreds of years as a source of phosphorite.

Photosynthesis: A complex chemical process that occurs in plants, cyanobacteria and some species of bacteria. Carbon dioxide and water are converted into glucose with energy from sunlight being captured and stored in the chemical bonds between the carbon atoms. Photosynthesis can be summarised by the equation:

$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$
Carbon dioxide + water → Glucose + oxygen

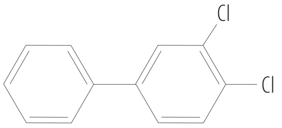
Plasticiser: A compound that increases the ability of a material to be deformed in shape.

Podzolisation: The mobilisation of organic matter and leaching of iron and aluminium from the topsoil into the B horizon of soils. This movement results in a bleached A horizon and a darker B horizon. Podzolisation usually occurs in acid soils in humid, temperate climates and often under forests.

Polarity: The separation of electric charge in a molecule so that one region has a net positive charge and another region a net negative charge. Some molecules or functional groups are called non-polar as they have no net electric charge.

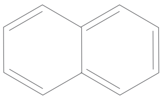
Polyacrylamide: A synthetic polymer that can flocculate solids dispersed in a liquid. Water-soluble polyacrylamides are used as soil conditioners to control erosion.

Polychlorinated biphenyl (PCB): A group of over 200 organic compounds produced by the chlorination of the biphenyl molecule, two benzene rings joined together. PCBs were produced commercially until the late 1970s and were used in a number of products such as electrical equipment, paints, plasticisers and lubricants. PCBs have a range of toxicities and can cause cancer as well as affecting the immune and reproductive systems.



3,4-Dichlorobiphenyl

Polycyclic aromatic hydrocarbon (PAH): A complex class of organic compounds containing two or more aromatic rings fused together and containing only carbon and hydrogen atoms. Naphthalene is the simplest of the PAH compounds. PAHs are found in oils, tars and coal and are released into the atmosphere as by products of burning fossil fuels and biomass. They are also found in cooked foods. Some PAHs may cause cancer, genetic mutations and birth defects.



Napthalene

Polyelectrolyte: A large molecule (polymer) with repeating structural units, that each carry an electrolyte group. These groups dissociate in water leaving a net charge on the polymer. If some of the hydrogen ions bound to the polymer are donated into the solution it is called a weak acid polyelectrolyte.

Polyfunctional compound: Organic molecules that have more than one functional group, resulting in a range of chemical properties that may be interrelated.

Polyphenols: A class of organic compounds with multiple phenol units.

Polysaccharide: Carbohydrates made up of repeating units of single (monosaccharide) and double (disaccharide) sugars.

Polysaccharide gum: Polysaccharides that, when added to a solution, cause it to become more viscous or to thicken. Among other uses, polysaccharide gums are used as emulsifying and flocculating agents.

Polyvalence/Multivalence: Ions with two or more valence bonds.

Polyvinyl alcohol: A water-soluble synthetic polymer that can form films and has strong emulsifying and adhesive properties. Polyvinyl alcohols have been applied to degraded soils to reduce runoff and soil loss caused by erosion.

Potable water: Water that is drinkable – that is, not contaminated by pathogens, vectors, toxins or high levels of minerals or suspended solids.

Protein: A class of nitrogenous macromolecules made up of one or more polypeptides. Each protein is folded into a specific three-dimensional shape. Proteins make up a large portion of all organisms and are essential for all of life's processes.

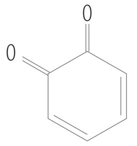
Proton pump: A protein that is permanently attached to a cell membrane, moving protons (H^+) across that membrane to create an electrochemical gradient. This gradient is used as an energy source for the secondary transport of molecules and ions across the membrane.

Putrefaction: The decomposition of organic matter, especially protein, by microorganisms that results in the production of an offensive odour.

Pyrogenic: Produced by or producing heat.

Pyrolysis: Decomposition of organic material at high temperatures in the absence of oxygen.

Quinones: A class of organic compounds derived from aromatic units such as benzene where an even number of C-H groups are converted into C=O groups.



1,2-Benzoquinone

Recalcitrant/Refractory: When referring to organic compounds, those that can resist microbial degradation.

Redox reaction: An abbreviation for oxidation-reduction reactions. Redox is a family of reactions in which there is a transfer of electrons between the reactants. Oxidation results in the loss of electrons and reduction, the gain of electrons. The two must always occur hand-in-hand, each individual reaction being referred to as a half-reaction. An example is the oxidation of iron in soils:

$4Fe^{2+} + O_2 \rightarrow 4Fe^{3+} + 2O^{2-}$
Oxidation half-reaction: $4Fe^{2+} \rightarrow 4Fe^{3+} + 4e^-$
Reduction half-reaction: $O_2 + 4e^- \rightarrow 2O^{2-}$

Red podzol: Acidic soils that occur in humid climates, usually with a rainfall of more than 650 mm. Red podzols have a light textured, pale A2 horizon with a heavier textured, structured B horizon that is red in colour from the leaching of iron oxides down through the profile.

Respiration: A complex sequence of metabolic reactions that take place in cells to convert biochemical energy into ATP. Respiration can be summarised by the equation:

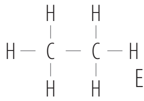
$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$
Glucose + oxygen → Carbon dioxide + water

Rhizosphere: The area immediately surrounding the roots of plants that is directly affected by root secretions and associated microorganisms.

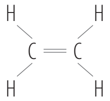
Saltpetre: Usually refers to potassium nitrate but may also refer to sodium, calcium or magnesium nitrates.

Saprophytic: The breakdown of dead or decayed organic matter by extra-cellular enzymes produced by fungi and bacteria.

Saturated compound: An organic compound with no double or triple bonds between the carbon atoms. The degree of unsaturation determines the number of hydrogen bonds that can bind to a compound.



Ethane (saturated)



Ethene (unsaturated)

Slaking: The breakdown of soil aggregates into smaller micro-aggregates when the soil is immersed in water. As the water is absorbed into the aggregate the air in the soil pores is compressed. If the aggregate does not have sufficient mechanical strength, the increased air pressure will shatter (or slake) the soil aggregate into smaller particles. Slaking can occur with or without dispersion.

Sodic soil: A soil containing a high concentration of sodium that affects soil stability and/or plant growth.

Soil enzymes: Biological catalysts in the soil produced by plant roots and microorganisms.

Soil fauna: Animals that live in soil.

Soil remediation: The removal of harmful contaminants in a soil.

Solid-state NMR: A type of nuclear magnetic resonance spectrometry used to determine the structure of large insoluble molecules such as crystals and molecular aggregates.

Sorption: The process where one substance becomes attached to another by chemical and physical means.

Spectrometry: An analytical technique that measures the characteristics of individual molecules of an element. In mass spectrometry (MS) a sample is vaporised and ionised and then the ions are sorted and separated by magnetic and electric fields. MS is used to determine the molecular mass of a sample as well as its elemental composition and chemical structure.

***Spirodella* spp.**: A genus of aquatic plants, commonly called duckweed.

Stearic acid: A saturated fatty acid with an 18-carbon chain, found in many animal and vegetable fats and oils.

Stomatal conductance: The rate of movement of carbon dioxide into and water vapour out of a leaf via the stomates, small pores on the surface of leaves that open and close allowing gases to pass in and out.

Suberin: A waxy substance produced by plants to prevent water from penetrating plant tissue. Suberin is found in bark and is the main component of cork.

Substrate: A substance that undergoes a chemical reaction.

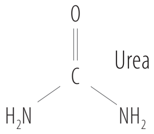
Sulphide: An anion of sulphur with the valence of 2 minus (S^{2-}).

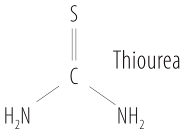
Supramolecular mixture: Smaller molecules held together in a larger assembly by non-covalent interactions such as hydrogen bonding, hydrophobic forces and van der Waal's forces.

Surfactant: A compound that lowers the surface tension of a liquid.

Tannins: A group of polyphenolic compounds with a bitter and astringent taste produced by plants. Tannins help to protect plants from predators.

Thiourea: An organosulphur compound with the formula $SC(NH_2)_2$. Thiourea is structurally similar to urea, except that the oxygen atom in urea is replaced by a sulphur atom in thiourea. Despite the structural similarity, the properties of urea and thiourea differ significantly.


Urea


Thiourea

Torfic acid: An early name for humic acid, first extracted by Hermann in 1841.

Transition metals: Metals placed in the middle section of the periodic table that exhibit more than one oxidation state due to the arrangement of the electrons around the nucleus of their atom. For example, iron is found as Fe^{2+} in an oxygen poor environment such as a waterlogged soil but is oxidised to Fe^{3+} when the soil dries out.

Turnover time: A measure of the age of organic matter in soils – the time taken to completely empty the reservoir if there are no new inputs.

Typic Haplustalf: A soil that belongs to the order Alfisol and suborder Ulstalf in the USDA Soil Taxonomy. These soils form in semiarid to subhumid climates often under hardwood forests. They have a fine; loamy texture with a clay enriched subsoil and are only moderately leached with a base saturation of more than 35% and a relatively high native fertility.

Ulmic acid: An early name for humic acid, first extracted in the 1840s.

Ulmin: A term coined in the late 1700s for black preparations extracted with alkali from soils, peats, coals and plants.

Ultraviolet (UV)- visible spectrometry: A spectrometry technique that measures how a sample absorbs and reflects visible and ultraviolet wavelengths of light. It is used to determine quantities of organic compounds, biological macromolecules and transition metals.

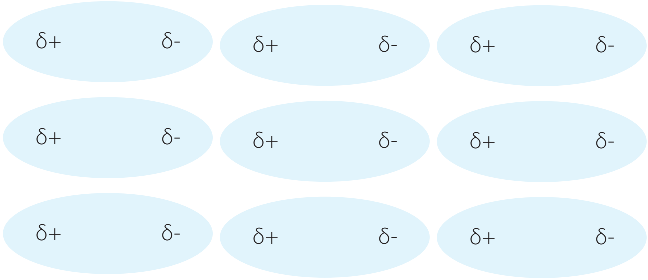
Unlithified sediments: Soft sediments that have little strength and can be easily deformed by the pressure of a fingernail or broad blade of a knife or spatula.

Unpaired electron: An electron of one atom that is available to form a bond with another atom. Most electrons that orbit the nucleus of an atom do so in relatively stable pairs. Unpaired electrons enable chemical reactions to occur between atoms, ions and molecules.

Urease: An enzyme that catalyses the hydrolysis of urea into carbon dioxide and ammonia.

Valency: The number of bonds that can be formed by an atom or ion of a given element. Sodium (Na^+) and potassium (K^+) have a valence of 1 and can each form one bond with another ion. Carbon has a valence of 4, with each carbon atom capable of forming four bonds.

Van der Waal's forces: Relatively weak attractions between molecules caused by the constant rearrangement of electrons in atoms. Electrons are continually orbiting around the nuclei of atoms. At any point in time there are likely to be more electrons on one side of an atom or molecule than on the other side creating a temporary dipole – one side is more electrically positive (δ+) and the other side more electrically negative (δ-). A temporary dipole in one molecule can induce another temporary dipole in a neighbouring molecule and so on. A whole lattice of molecules can be held together as a solid using van der Waal's forces.



Van der Waal's forces holding atoms together in a lattice

Vermicompost: An organic fertiliser and soil conditioner produced by various species of worms using decomposing organic material as a food source.

Vermiculite: A very soft, clear to brown clay found in soils, formed from the weathering of biotite and magnesium micas. Considered to be a coarse-grained montmorillonite, vermiculite is also a 2:1 clay made up of layers of one alumina sheet sandwiched between two silica sheets. It has a medium shrink-swell capacity and a high content of bases and high CEC.

X-ray analysis: An analytical technique used to determine the arrangement of atoms in a sample. When a beam of x-rays strikes the atoms they diffract or bend in many specific directions. A three-dimensional picture is produced from the angles and intensities of the diffracted beams.

Xenobiotic: A chemical compound that is found in, but foreign to, a particular organism. Xenobiotics include drugs such as antibiotics, pesticides and industrial pollutants. They may or may not be harmful to an animal's system.

Xylem: Transport tissues in vascular plants that conduct water and nutrients from the roots up into the plant.

Water-soluble organics: Organic compounds that dissolve in the soil solution and have known molecular structures such as polysaccharides, sugars, proteins and amino acids.

Waxes: A group of organic compounds that are plastic, that is, can change shape, at ambient temperatures. In warm climates, plants produce waxes to reduce evaporation from leaf and stem surfaces.