Chemical saviours

The discovery and development of selective herbicides for turf.
By Graham Paul

Selective herbicides used to kill broad-leaved weeds in turf were developed from agricultural chemicals. Much of the first part of this article deals with the search for weed control in cereals, which are members of the same botanical family as grasses; the Gramineae. Therefore, the situation in amenity is the same as in agriculture, in that we are trying to control unwanted dicotyledonous plants in a monocotyledonous crop.

The use of chemicals to kill vegetation is not new; the first examples in history date back to around 1200BC when conquering armies, in what we now call the Middle East, used salt and ash to wipe out their enemy's crops. In effect, these were chemicals used to spite others; the beneficial use of chemicals took much longer to emerge.

In mid nineteenth century Germany, a mixture of sulphuric acid and iron sulphate was used in possibly the first selective weed control experiment in European agriculture.

However, it was not until later in the 19th century that the early beginnings of the herbicide industry started to have an impact on agricultural practices.

The first products to come to market were copper salts that were found to provide a degree of selective weed control in cereal crops and boost the yield.

About a dozen other metal salts including such efficacious offerings as iron sulphate and sodium nitrate soon followed to add to the product portfolio!

These metal salts had a contact action against the broad-leaved weeds, killing the aerial growth but leaving the roots intact, which could allow weed re-growth to occur in many cases.

Selectivity was partly due to differences in spray retention on the leaf between the crop and target. The finer, upright leaves of the cereal plants have a waxy coating and therefore retain less of the chemical than the leaves of broad-leaved weeds; which are rounder, have a greater surface area and are often horizontally oriented.

Also, the growing tips of cereals and grasses are less vulnerable to sprays, being located in the base of the plant and protected by older leaves, whereas those of broad-leaved plants are terminal and more exposed to attack by chemicals.

Broad leaved weeds present a rounder, wider, horizontal target

These early selective herbicides were slow to be taken up by farmers due to the high cost of the active ingredients and their relatively poor cost/benefit – without modern formulation technology the performance was erratic and the salts could be easily washed away by heavy rainfall before the full effect was seen.

The long-term use of certain metal salts, e.g. copper sulphate, could also lead to the build-up of toxic residues in the soil that would eventually reduce the crop vigour.

However, one positive thing that emerged from these early agrochemicals was that they established the concept of chemical weeding and encouraged research into finding a more reliable means of achieving it.

In the 1930's a team of scientists working for ICI at the Jealott's Hill Research Station were working on a project to eradicate weeds in cereal crops by spraying with sulphuric and other acids.

The report published by G.E. Blackman and W.G. Templeman in 1936 showed up to 90% control of Charlock and Wild Radish in cereal crops sprayed with 9.2% sulphuric acid and slightly better control with similar concentrations of nitric acid.

It took a few more years of research and the sudden pressing need to feed a world at war, for the real breakthrough to come.

This was the introduction of the hormone herbicide 2,4-D, developed by a British team at Rothamstead Experimental Station in Hertfordshire led by Judah Hirsch Quastel. 2,4-D was the first of the group known as the phenoxy or hormone herbicides whose activity was due to its chemical similarity to naturally occurring plant growth hormones.

The use of phenoxy herbicides causes the plant to undergo uncontrolled growth, resulting in twisting of the leaves and stems – a symptom known as 'epinasty' where one surface of the leaf or one side of the stem grows faster than the other.

Only dicotyledonous plants are affected by the phenoxy herbicides, monocotyledonous plants such as cereals and grasses are largely unaffected – although a very high dose will cause scorching in monocots.

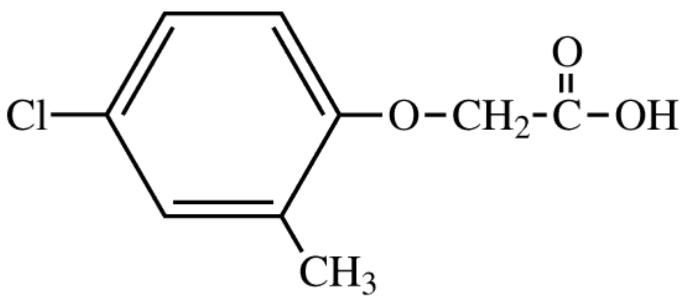
2,4-D was released commercially in 1946 and was quickly followed by several other similar products from the same chemical group– some of which will be familiar to those working in the amenity turf industry; MCPA, 2,4-DB, dichlorprop, fenoprop, mecoprop and 2,4,5-T.

Many of these herbicides found uses in weed control in the main monocotyledonous crops throughout the world; cereals, maize and rice. Selective turf herbicides came a little later, borrowing the technology from the larger agricultural market.

The chemical structures of the phenoxy herbicides are very similar but small differences can dramatically change the spectrum of weeds they control.

For example MCPA and mecoprop differ only in the replacement of one hydrogen atom (H) in MCPA with a methyl group (CH3).

MCPA is generally more effective on the deeper rooting weeds such as Dandelion, Docks and Cat's-ear whilst mecoprop gives better control of many smaller leaved weeds such as White Clover, Black Medick, Common Chickweed and Procumbent Pearlwort. By careful mixing of two or more active ingredients in a single product, manufacturers have been able to extend the weed spectrum in a bid to provide a complete answer to weed problems in one spray application.



One early example of this was 'Supertox' (now withdrawn) from May & Baker, which combined 2,4-D and mecoprop to control 18 out of the 22 commonly occurring turf weeds in the UK. It served the amenity market for some 40 years before disappearing in 2009 having been superseded by the newer products such as the 3 way mixes with dicamba, MCPA and mecoprop-P, which offer a slightly broader weed spectrum.

The suffix –P that appears after mecoprop denotes the use of an isomeric form of this molecule. When certain chemicals are manufactured, the end product can be a mixture of two stereoisomers of the desired molecule.

Without going into great detail, the best way to illustrate stereoisomers is to look at your left and right hands. They are mirror images of one another, having the same number of fingers and thumbs attached to the palm in a similar but opposite way.

The manufacture of mecoprop produces a mixture of two molecules known as the '-' and '+' isomers; i.e. both left and right handed forms of the same chemical.

Both isomers will have the same physical and chemical properties. However, in nature usually only one isomeric form of a molecule is produced so when a pesticide works by mimicking a natural product, such as a plant growth hormone, it follows that a mixture of the '-' and '+' isomers will have only half of the activity of a pure solution of the one that is closest to natures genuine part.

Modern chemical technology now allows us to manufacture mecoprop that contains only the '+' isomer (mecoprop-P) so we can reduce the amount of chemical applied to the environment without losing the effectiveness of the product.

The period from the end of the Second World War through to the 1980's saw exponential growth in the discovery and development of new herbicides with companies investing heavily in screening and development programmes aimed at finding new active ingredients.

In addition to the phenoxy hormone herbicides, several other important selective herbicides used on turf and grassland were discovered including; dicamba, triclopyr, asulam and the hydroxybenzonitrile (HBN) herbicides ioxynil and bromoxynil.

Dicamba and triclopyr are also described as 'plant hormone' herbicides but belong to a different chemical group. The HBN herbicides work by interfering with pho-

tosynthesis, a process that occurs in both grasses and broad-leaved vegetation. Selectivity is achieved by this group because grasses can rapidly break up the herbicide as soon as it enters the plant and before it reaches the target.

The mode of action of asulam is not fully understood but researchers believe that selectivity comes from rapid degradation of the chemical in the same manner as the HBN herbicides.

The rate of discovery of new herbicides slowed during the latter part of the 20th century with increased public awareness and concerns about environmental and health issues.

Increasing pesticide legislation and food surpluses also helped to apply the brakes. European Council Directive 91/414/ECC was issued to harmonise national arrangements for authorising pesticides within the EEC.

It resulted in the removal of two thirds of the active ingredients from the approved chemicals list in the UK by the time the exercise was completed in 2009.

Thankfully we still have a trickle of new chemicals getting through these tight controls. In recent years we have seen the introduction of products containing florasulam, fluroxypyr and carfentrazone, which have all found a place in this ever changing market.

Probably the most infamous 'chemical hoe' and member of the phenoxy group is the herbicide 2,4,5-T, whose activity as a brushwood killer took it into the service of the American Forces fighting in the jungles in 1960's Vietnam.

The product, known as 'Agent Orange', was a mixture of 2,4-D and 2,4,5-T.

This was applied to large areas of Vietnam to remove the cover provided by the jungle. Over the 10 years of the campaign in Vietnam a staggering 77 million litres of the defoliant was sprayed, so it had to be manufactured as quickly and cheaply as possible. The side effects of exposure to 'Agent Orange' started to emerge after a few years of spraying.

Studies showed a dramatic increase in horrific birth defects in children and skin problems in adults living in the treated areas. Researchers soon found out that it wasn't 2,4-D or 2,4,5-T that caused these effects but highly toxic bi-products of their manufacture known as dioxins.

Today, such impurities are removed to ensure that the commercial product is safe enough to use but in the 'military policing action' in Vietnam, the US Forces had neither the time nor the budget to produce a clean product. Many books have been written on the side effects of 'Agent Orange' because it affected so many people from both sides of the conflict.

It is fairly safe to say that the eventual withdrawal of the herbicide 2,4,5-T in the 1980's was in part due to the high levels of publicity that arose from its use in Vietnam.

SELF ASSESSMENT

Use the questions below to check your understanding of this topic. Readers can claim two BASIS points if the questions are answered correctly, by filling in the form at:
www.sherriff-amenity.com/technical.asp?newsid=21
Circle the correct answer(s)

1) When was the herbicide 2,4-D first released commercially?
a) 1896 b) 1940 c) 1946 d) 1964

2) How do 'hormone' type herbicides kill broad-leaved weeds?
a) Interfere with growth processes in the target plant.
b) Prevent transpiration causing loss of cooling.
c) Corrode aerial parts of the weed.
d) Poison the growing tips.

3) The suffix –P given to some selective herbicides such as mecoprop-P denotes: -
a) Professional formulation for use by certified spray operators only.
b) It contains only the active (+) stereoisomer.
c) Pure formulation – containing no dioxins.
d) Poisonous to bees.

4) The disfigurement of leaves and stems caused by all hormone type herbicides is known as: -
a) epiphany b) contracture c) epinasty d) exogamy

5) What is the mode of action of the HBN herbicide ioxynil?
a) Inhibits cell elongation
b) Inhibits DNA replication in target plants.
c) Interferes with photosynthesis
d) Causes uncontrollable growth

6) In the report published by G.E. Blackman and W.G. Templeman in 1936, what weed species were involved in their experiments?
a) Chamomile and Wild Rocket
b) Cleavers and Wild Carrot
c) Corn Marigold and Wild Oats
d) Charlock and Wild Radish

References:
1) G. E. Blackman and W. G. Templeman (1936). The eradication of weeds in cereal crops by sulphuric acid and other compounds. The Journal of Agricultural Science, 26, pp 368-390