Herbicide Group A modes of action

Herbicide resistance is caused by the intensive use of herbicides for weed control. A small number of weeds can be naturally resistant to herbicides, even before the herbicides are used. When a herbicide is used, these individual weeds can survive and set seed, whereas the majority of susceptible plants are killed. Continued use of a herbicide or herbicide group will eventually result in a significant number of the weed population developing resistance.

One of the most important methods for preventing, delaying, or managing resistance is to reduce the reliance on a single herbicide MOA. To do this, growers must be aware of the MOA for the herbicides they intend to use, but the relatively complex nature of plant biochemistry makes this difficult to determine. Therefore, a classification system for herbicides based on their mode of action to the herbicide has been developed.

The Group A Mode of Action (MoA) herbicides are also called ACCase (acetyl co-enzyme A carboxylase) inhibitors. They are classified as Group A by the global Herbicide Resistance Action Committee (HRAC) and Group 1 by the Weed Science Society of America (WSSA) (http://hrac.tsstaging.com/tools/classification-lookup).

There are three chemical classes within the Group A MoA as shown in Table 1. These classes are different types of chemicals; however, they affect the same biochemical pathways in the plant.

The MOA table and the herbicide resistance management strategies with their specific guidelines can be found on the CropLife Australia website www.croplifeaustralia.org.au.

To facilitate management of herbicide resistant weeds, all herbicides sold in Australia are grouped by MOA which is indicated by a letter code on the product label. It is displayed on the front panel of the label in a box as such:

Group **G** **Herbicide**

Group A herbicides are primarily active on grasses (monocots) and a limited number of broadleaf (dicot) weeds. This selectivity occurs because Group A herbicides cannot bind to the ACCase enzymes of most broadleaf plants.

Table 1: *Herbicides included in Group A.*

Chemical class	Active ingredient	Product examples
Aryloxyphenoxypropionates ‘fops’	Clodinafop	Topik®
	Cyhalofop	Barnstorm®
	Diclofop	Halley Diclofop Herbicide, Cheetah® Gold
	Fluazifop	Fusilade®
	Haloxyfop	Verdict®
	Propaquizafop	Shogun®
	Quizalofop	Targa®
Cyclohexanediones ‘dims’	Butroxydim	Factor®
	Clethodim	Select®
	Profoxydim	Aura®
	Sethoxydim	Sertin®, Cheetah® Gold, Decision®
	Tralkoxydim	Achieve®
Phenylpyrazoles ‘dens’	Pinoxaden	Axial®

Cheetah® Gold, Decision® and Axial® contain more than one active constituent.

Source: http://www.croplife.org.au/resistance-strategy/herbicide-mode-of-action-groups/

2A.1 Mode of action and biochemical pathways

Group A herbicides block ACCase, the first enzyme in the production of fatty acids. This process primarily occurs in the chloroplasts. Stearic acid (16 carbon atoms) and palmitic acid (18 carbon atoms) are produced and released to the cell fluid (cytoplasm) and are essential components of cell and chloroplast membranes.

These fatty acids are also used as building blocks for suberin, cutin and waxes. Suberin is a long-chain waxy material found in plant cell walls, the endodermis (the Casparian strip), and the cuticle. Cutin is a waxy, transparent material in the cuticle of plants that contains highly polymerised esters of fatty acids.

Blocking ACCase halts the manufacture of cell membranes, which is necessary for cell growth.

Most of this activity occurs in the meristem in the base of actively growing leaves and the crown region of the plant. Group A herbicides slow and stop growth in these regions leading to senescence and eventually tiller death.

For a detailed explanation go to: Plant & Soil Sciences eLibrary Lessons: Inhibitors of fatty acid synthesis and elongation.

Photo 1: *Researchers carrying out herbicide resistance trial work.*

Source: GRDC

2A.2 Absorption into the plant

Group A herbicides are absorbed primarily via the leaves; however, diclofop and dims are also absorbed through the roots under certain conditions.

Group A herbicides are lipophilic, penetrating the cuticle and entering the leaves quickly. Because most Group A herbicides have very low solubility in water (Table 2), they are formulated as emulsifiable concentrates in an organic solvent so they will mix with water.

Fops are also formulated as 'pro-herbicides' by adding a methyl, ethyl or butyl ester group to the acid form. This assists absorption through the cuticle. Like Group I herbicides, fops are converted to the active form (acid) once inside the plant.

Dims and dens do not need to be formulated as pro-herbicides to enter the plant.

Table 2: *Environmental characteristics of Group A herbicides.*

Group A class	Active ingredient	Example trade name	Water solubility (mg/L)	Log K_{ow}	Persistence in soil (half-life @ 20°C) (days)	Soil mobility (K_{oc}/K_{foc})	Breakdown by light under moist conditions
Aryloxyphenoxypropionates (fops)	Diclofop-methyl ester	Halley Diclofop Herbicide	0.4	4.8	10–30 (acid)	20,870, non-mobile	Slow
	Clodinafop-propargyl	Topik®	4 (acid)	3.9	5–20 (acid)	1466, slightly mobile	Fast
	Haloxyfop-p-methyl	Verdict®	7.9	4	55	Rapid degradation, no data	Slow
	Quizalofop-ethyl	Targa®	0.61	4.61	1.8	540, slightly mobile	Stable
Cyclohexanediones (dims)	Clethodim	Select®	>3000 (pH 5)	4.14	28 (pH 5) 300 (pH 7)	22.7, mobile	Fast
	Sethoxydim	Sertin®	4700	1.65	5	75, moderately mobile	Fast
	Tralkoxydim	Achieve®	6.1	2.1	2	120, mobile	Moderate
Phenylpyrazoles (dens)	Pinoxaden	Axial®	200		0.6	349, moderately mobile	Slow

Log K_{ow}, ratio of herbicide that is soluble in octanol (organic solvent) v. water; it is a good indicator of the lipophilic or hydrophilic nature of a herbicide; larger the log K_{ow} value the more lipophilic the herbicide; herbicides with values between –1 and 1 should move in the phloem following foliar application. K_{oc}/K_{foc}: >1000, binds strongly to soil; <500, moves in water. Solubility will vary with temperature and to a lesser degree pH.

Source: Pesticides Properties Database, http://sitem.herts.ac.uk/aeru/ppdb/en/index.htm

2A.3 Translocation within the plant

Group A herbicides are weak acids. Weak acids are compounds containing a functional group, usually a carboxylic acid. This functional group gains or loses a hydrogen ion (H+) depending on the pH of the surrounding solution.

The plant cell cytoplasm has a higher pH (~7.5) than the outside of the cell because the cell membrane pumps H+ ions through the cell wall. Weak acid herbicides are more fat-soluble (lipophilic) when outside the cell, owing to the lower pH. This helps weak acid herbicides to move through the cell membrane. Once inside the cell, the herbicide molecule becomes ionised (i.e. it loses an H+) and is trapped in the cell as it becomes more water-soluble and cannot pass back through the cell membrane.

Although fops and some dims are weak acid herbicides, movement within the plant is slow and limited because of their low water solubility. Fop movement through the plant is primarily via the phloem (symplast); however, dims move via both phloem and xylem (apoplast) (see box text for definitions).

They rapidly diffuse across the cell membrane (plasmalemma) but then they become trapped within the phloem cells.

Symplastic movement (the symplast is the network of all parts of the plant that have a membrane, including the phloem):

- Movement of water and solutes through the continuous connection of cytoplasm (via plasmodesmata).
- No crossing of the plasma membrane once it is in the symplast; however, if the solute was initially external to the cell, then it must have crossed one plasma membrane to enter the symplast.

Apoplastic movement (the apoplast is the space outside the plasma membrane, including cell walls and intercellular material):

- Movement of water and solutes through the cell walls and the intercellular spaces.
- No crossing of the plasma membrane.
- More rapid; less resistance to the flow of water.
- The xylem is part of this system because it is composed primarily of non-living cells (tracheids and xylem vessels).

2A.4 Symptoms

Growth ceases quickly following foliar application on small plants and more slowly on tillered plants. New leaf sheaths turn yellow and eventually brown. Shoot meristems die, and can best be observed by gently tugging the newest leaf, which should pull out and be yellow to brown.

Photo 2: *Group A symptoms, new leaf pulls out easily from the crown*

Photo: author unknown, GRDC Herbicide Damage Ute Guide

Photo 3: *Ryegrass showing Clethodim damage*

Photo: Chris Preston

Photo 4: *Axial banding in wheat*

Phot: Trevor Klien, Syngenta

Photo 5: *Group A damage showing death of the newest emerging leaf*

Photo: Andrew Storrie, Agronomo

Leaves turn bluey green, with older, fully formed leaves turning orange to red followed by general plant death. Older, well-tillered plants can often look unaffected until the youngest leaf in a tiller is gently pulled out to reveal the dead meristematic area at the leaf base.

2A.4.1 Timeframe for symptoms and plant death

Rate of development of symptoms and subsequent damage and death depend on plant species, herbicide dose, age and size of plant, and rate of plant growth. Death occurs from as early as two weeks to around four–six weeks post-application.

2A.5 Crop selectivity

Most dicots have an ACCase enzyme that does not allow the binding of Group A herbicides. The exception is *Erodium* spp., which are sensitive to haloxyfop. Limited research has also demonstrated that many species from the family Geraniaceae are sensitive to haloxyfop.

There is variation with respect to which species are controlled by different Group A herbicides. Group A herbicides do not control winter grass (*Poa annua*) or silver grass (*Vulpia* spp.). Generally, fops have more activity on volunteer cereals, annual ryegrass, barley grass, brome grass and wild oats. Dims, on the other hand, have more activity on summer grasses.

Cereal crops are tolerant of a range of Group A herbicides (Table 3), and there is rapid metabolism of the herbicide to nontoxic compounds. Often a 'safener' such as mefenpyr-diethyl is combined with the herbicide; safeners boost the levels of cytochrome P450, increasing the herbicide metabolism within the crop plant. Research has shown that the level of cytochrome boosting by safeners varies between wheat cultivars. A similar effect has been found in some fop herbicides by adding MCPA or a sulfonylurea (Group B) herbicide to the tank mix.

Several Group A herbicides are also toxic to cereal crops because they are not metabolised by P450 enzymes (see Table 3).

The breakdown compounds of sethoxydim are also phytotoxic, so they too have herbicidal activity. Breakdown products of most Group A herbicides are not phytotoxic.

Table 3: *Differences in selectivity between Group A chemical classes.*

Herbicide	Selective in some small-grain cereals	Non-selective in small-grain cereals
Fops	Clodinafop-propargyl	Fluazifop-p
	Cyhalofop-butyl (rice)	Haloxyfop-r
	Diclofop-methyl	Propaquizafop
Dims	Profoxydim (rice)	Butroxydim
	Tralkoxydim	Clethodim
		Sethoxydim
Dens	Pinoxaden	

2A.6 Soil activity

Although rarely noted on product labels, it has been known since the commercial release in the late 1970s of Group A herbicides that they have soil activity under certain conditions. Group A herbicides applied to bare dry soil a short time before sowing have been found to kill emerging cereal crops.

The level of soil activity is mediated by:

- herbicide type—significant differences between Group A herbicides
- herbicide rate—the higher the rate the better the control
- soil texture and pH—soils with lower proportion of clay will have more herbicide activity
- weed-crop density—interception of herbicide affecting soil activity
- photodecomposition—amount of light breaking down herbicide
- microbial breakdown—amount of soil moisture for microbes
- low water solubility—will keep herbicide near the surface.

Glasshouse experiments investigating the soil activity of foliar-applied fluazifop at two rates on barnyard grass (*Echinochloa crus-galli*) and at two densities (three and 50 plants per pot) found that herbicide interception with vermiculite (on the surface of the potting soil) reduced control by 51–18% at three plants per pot and by 22–19% at 50 plants per plot. The level of control was influenced by herbicide rate at both weed densities in the vermiculite treatments. Herbicide rate had less effect at the higher weed density, with more herbicide being intercepted and giving lower control at both herbicide rates.

Soil-absorbed diclofop and dims prevent growth of the primary root, and leaves fail to emerge from the coleoptile. Larger plants will have some inhibition of root growth.

2A.7 Effect of environmental conditions on activity

Group A herbicides are oil-soluble (lipophilic), so are rapidly absorbed by the leaf cuticle. However, owing to their low solubility in water, the rate of translocation within the phloem is slow.

2A.7.1 Light

High light conditions can thicken the cuticle of a weed, which will absorb a large proportion of the lipophilic herbicide. Dim herbicides are rapidly decomposed by ultraviolet light and are decomposed within a few days.

A decrease in light intensity, such as in autumn, increases the ratio between shoots and rhizomes in perennial species, which leads to better control through better herbicide interception and to more herbicide translocating to the root system. There is also an increase in the amount of assimilates moving into roots and storage organs, which in turn increases the transport of phloem mobile Group A herbicides.

2A.7.2 Temperature

As temperature increases, the rate of uptake of herbicide increases provided respiration and photosynthesis are not limited by the conditions. However, the total amount of herbicide absorbed by the plant does not change. High temperatures and low available soil moisture reduce herbicide translocation through the shutdown of transpiration.

Optimum temperatures for photosynthesis and respiration are determined by whether the plants use C3 or C4 photosynthesis. C3 plants grow best at temperatures <30°C, whereas C4 plants can actively grow at temperatures up to 35°C and at higher light intensities.

Frost can shut down plant growth for several days, leading to increased crop damage. The Achieve® label specifies not to apply to weeds or crops under stress due to severe frost. Increased crop damage results from lower production of P450 enzymes due to reduced crop growth, so that the herbicide is deactivated more slowly within the crop plant.

Analysis of 59 experiments investigating the efficacy of clodinafop-propargyl on wild oats (*Avena* spp.) showed that the level of weed control was strongly influenced by:

- the sum of the minimum temperatures for the seven days before spraying
- maximum temperature on the day of spraying.

The analysis found that the effect of low temperature stress on efficacy could be lessened by increasing the herbicide rate and application volume. Increasing the application volume should also improve spray coverage.

2A.7.3 Humidity

The main effect of humidity with Group A herbicides is the likelihood that weeds will be actively growing and will translocate the herbicide to the meristems. This assumes adequate soil moisture. High humidity and low soil moisture will slow transpiration and therefore photosynthesis and growth reducing levels of control.

2A.7.4 Soil moisture stress

Stressed plants have thicker cuticles that will absorb and retain more Group A herbicides. Moisture stress will reduce translocation of the herbicide and reduce herbicide efficacy. Addition of certain adjuvants can assist herbicide absorption into the plant; however, if it is not actively growing, translocation and efficacy will be limited. Analysis of clodinafop efficacy trials mentioned above also showed that by increasing herbicide rate and application volume (i.e. spray coverage), soil moisture stress could be partially overcome.

MORE INFORMATION

See the comprehensive GRDC Spray Application GrowNote for more information.
https://grdc.com.au/Resources/GrowNotes-technical/Spray-Application-Manual

Sufficient soil moisture is also required for the rapid microbial breakdown of these herbicides.

2A.7.5 Rainfall

Group A herbicides can be rain-fast anywhere between 30 minutes and several hours. This is also likely to vary with weed species, depending on the amount epicuticular wax present on the leaf.

Dew or light rain soon after application has been known to increase crop damage because herbicide runs into the leaf axils, increasing the quantity absorbed. This can overwhelm the enzymes responsible for metabolising the herbicide before it reaches the meristem, leading to crop damage.

2A.8 Spray application

Because of the slow translocation of Group A herbicides within the plant, good spray coverage is essential.

Label recommendations vary from specifying a minimum application volume of 50 litres per hectare to specifying that no less than 50% of the droplets are in the range 150–300 microns. Others specify 110° nozzles and warn about the use of air induction nozzles, hollow cones and flood jets.

The Factor® label recommends medium to coarse spray quality and addition of oil adjuvant.

Other labels suggest a fine–medium spray quality. All suggest increasing application volume with dense crops and weeds.

Recent research has shown that using a medium spray quality at 60–80 litres per hectare gives excellent coverage. Medium spray quality will also have better penetration of crop and weed canopies than fine spray quality. Use of fine spray quality without air-assist is likely to lead to the off-target loss of 50% of the spray.

2A.8.1 Adjuvants

All Group A herbicides require an adjuvant to improve their deposition and uptake. Most commonly, the preferred adjuvant is crop oil. Often if tank-mixing with a herbicide for broadleaf weeds, a non-ionic surfactant is recommended in place of crop oil to lessen potential crop damage.

Read the label for recommended use of adjuvants.

MORE INFORMATION

See the GRDC Adjuvants Booklet https://grdc.com.au/resources-and-publications/all-publications/publications/2015/04/adjuvants-booklet

2A.8.2 Water quality

Temperature

No data are available on the effect of low spray solution temperatures on efficacy.

pH

The effect of the pH of a spray solution is one of the most widely misunderstood concepts in spray application. The pH will have little effect on efficacy. Dropping the pH of a spray solution with an unbuffered product can lead to herbicide coming out of solution. Do not leave spray premixed overnight.

The water pH can affect a product's half life in the spray tank.

Hardness

Group A herbicides are weak acids and as such can be affected by hard water.

Dim herbicides are particularly sensitive to bicarbonate ions and concentrations as low as 250 ppm can severely impact on herbicide effectiveness.

If using bore water, or in an area with a lot of limestone, water should be specifically tested for bicarbonate. Bicarbonate will not be detected by normal hardness tests or hardness test strips.

Hardness can be largely counteracted by the use of ammonium sulfate dissolved in the spray water before the herbicide is added.

Turbidity

Muddy water with low levels of algae pose a risk of filter and nozzle blockage.

2A.9 Further reading

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Herbicide Group B modes of action

The Group B Mode of Action (MoA) herbicides are also called ALS (acetolactate synthase) inhibitors. They are also classified as Group B by the global Herbicide Resistance Action Committee (HRAC) and Group 2 by the Weed Science Society of America (WSSA) (http://hrac.tsstaging.com/tools/classification-lookup).

There are four chemical classes within the Group B MoA as shown in Table 1. These classes are different types of chemicals; however, they affect the same biochemical pathways in the plant.

Group B herbicides can be active on both grasses and broadleaf (dicot) weeds. They can be used for pre- and post-emergent weed control on a range of crops and pastures. Some are used in fallows and some for total vegetation control.

Table 1: *Herbicides included in Group B.*

Chemical class	Active ingredient	Product examples
Imidazolinones 'imis'	Imazamox	Intervix® (PM), Raptor®
	Imazapic	Flame®, Midas® (PM), OnDuty® (PM)
	Imazapyr	Arsenal® Xpress, Intervix® (PM), Lightning® (PM), Midas® (PM), OnDuty® (PM)
	Imazethapyr	Spinnaker®, Lightning® (PM)
Pyrimidinylthiobenzoates 'benzoates'	Bispyribac	Nominee®
Sulfonylureas 'SUs'	Azimsulfuron	Gulliver®
	Bensulfuron	Londax®
	Chlorsulfuron	Lusta®
	Ethoxysulfuron	Hero®
	Foramsulfuron	Tribute®
	Halosulfuron	Sempra®
	Iodosulfuron	Hussar® (CS)
	Mesosulfuron	Atlantis® (CS)
	Metsulfuron	Ally®, Stinger™ (PM), Trounce® (PM)
	Prosulfuron	Casper® (PM)
	Rimsulfuron	Titus®
	Sulfometuron	Oust®
	Sulfosulfuron	Monza®
	Thifensulfuron	Harass®
	Triasulfuron	Logran®
	Tribenuron	Express®
	Trifloxysulfuron	Envoke®

Chemical class	Active ingredient	Product examples
Triazolopyrimidines ‘sulfonamides’	Florasulam Flumetsulam Metosulam Pyroxsulam	Paradigm™ (PM), Vortex® (PM), X-Pand® (PM) Broadstrike™ Eclipse® Crusader™ (CS)

PM, Product contains more than one active constituent; some products listed contain two active ingredients from one chemical class. CS, Contains crop safener.

Source: http://www.croplife.org.au/resistance-strategy/herbicide-mode-of-action-groups/

2B.1 Mode of action and biochemical pathways

Group B herbicides block the ALS enzyme essential in the production of the branched-chain fatty acids (amino acids) leucine, isoleucine and valine. These amino acids are essential for the production of proteins and for normal plant growth, while also providing precursors for a number of secondary products such as cyanogenic glycosides, glucosinolates and acyl-sugars.

A detailed explanation of branched chain fatty acid synthesis can be found here at the Plant & Soil Sciences eLibrary: http://passel.unl.edu/pages/informationmodule.php?idinformationmodule=980466115&topicorder=2&maxto=4

This process occurs within the chloroplasts. Once the ALS enzyme is blocked, plant growth quickly stops with the cessation of cell division. There can also be a buildup of the intermediate molecule alpha ketobutyrate, which is toxic, plus a decrease in phloem transport. Group B herbicides can therefore self-limit their translocation within the plant.

2B.2 Absorption into the plant

Group B herbicides are weak acid herbicides with moderate water solubility (Table 2) and are absorbed via the leaves and the roots, using the aqueous pathway.

Table 2: *Environmental characteristics of Group B herbicides.*

Group B class	Active ingredient	Example trade name	Water solubility (mg/L)	Log K_{ow}	Persistence in soil (half-life @ 20°C) (days)	Soil mobility (K_{oc}/K_{foc})
Imidazolinones	Imazamox	Raptor®	626,000	5.36	17	Very mobile
	Imazapic	Flame®	2230	2.47	232	Moderate
	Imazapyr	Arsenal®	9740	0.11	11	Moderate
	Imazethapyr	Spinnaker®	1400	1.49	51	Mobile
Sulfonylureas	Chlorsulfuron	Lusta®	12,500	–0.99	36	Mobile
	Metsulfuron	Ally®	2790	–1.87	13	Very mobile
	Triasulfuron	Logranc	8015	–0.59	39	Very mobile
	Iodosulfuron	Hussar®	25,000	–0.7	3	Mobile
Sulfonamides	Florasulam	Paradigm™	6360	–1.22	9	Mobile
	Flumetsulam	Broadstrike™	5650	0.21	45	Mobile
	Metosulam	Eclipse®	700	0.2	39	Moderate
	Pyroxsulam	Crusader™	3200	–1.01	13	Mobile

Log K_{ow}, ratio of herbicide that is soluble in octanol (organic solvent) v. water; it is a good indicator of the lipophilic or hydrophilic nature of a herbicide; the larger the log K_{ow} value the more lipophilic the herbicide; herbicides with values between –1 and 1 should move in the phloem following foliar application. K_{oc}/K_{foc}: >1000, binds strongly to soil; <500, moves in water. Solubility will vary with temperature and to a lesser degree pH.

Source: Pesticides Properties Database: http://sitem.herts.ac.uk/aeru/ppdb/en/index.htm

2B.3 Translocation within the plant

Group B herbicides are weak acids. Weak acids are compounds containing a functional group, usually a carboxylic acid. This functional group gains or loses a hydrogen ion depending on the pH of the surrounding solution (for more details, see Herbicide GrowNotes: Group A).

Group B herbicides are readily transported within the phloem and xylem of plants, meaning that they are well translocated to the meristems of growing plants.

Sulfonylureas are preferentially transported in the xylem, and slower in the phloem, whereas imidazolinones are primarily transported in the phloem and less so in the xylem.

Sulfonamides are absorbed by the shoots and roots. Plants tolerant of the herbicide florasulam have reduced translocation from the leaves.

2B.4 Symptoms

Growth ceases quickly following foliar application on small plants and more slowly on larger plants. The initial symptoms include the yellowing of growing points. New upper leaves wilt. Mid-rib and veins of some dicots turn red. Plants that receive a sub-lethal dose remain stunted, often with a severely reduced root system.

Photo 1: *SU residue effects on canola seedling, note stunting and reddening.*

Photo: David Pfeiffer

Photo 2: *Glean effects, yellowing of growing point on Albus lupins.*

Photo: G. Shepard, IMAG Consulting

Photo 3: *Spinnaker causing growing tips to yellow on field peas.*

Photo: Penny Heuston

Photo 4: *Spinnaker damage in soybeans.*

Photo: DPI&F

Photo 5: *Group B damage on a radish plant.*

Photo: Andrew Storrie, Agronomo

MORE INFORMATION

YouTube video. Ohio State University Weed Science time lapse of the effect of the sulfonamide herbicide cloransulam on common cocklebur.

NSW DPI: Weed control in winter crops

Photo 6: *Metosulum damage to a faba bean plant 27 days after treatment.*

Photo: Andrew Storrie, Agronomo

2B.4.1 Timeframe for symptoms and plant death

Rate of development of symptoms and subsequent damage and death depend on the plant species, herbicide dose, age and size of plant, and rate of plant growth. Death occurs from as early as two weeks to around four–six weeks post-application.

Plants that have received a sublethal dose often live until they are exposed to moisture stress from increasing temperatures and drying surface soil.

2B.5 Plant selectivity

Selectivity in crops and weeds is due to rapid detoxification, and in some instances (e.g. florasulam) is aided by slow translocation from the leaves to the growing points.

There is a large variation in crop cultivar sensitivity to various Group B herbicides (Table 3). See the National Variety Trials Herbicide Tolerance web site for details.

Wheat, barley, canola and maize cultivars have been bred with additional tolerance to imidazolinone herbicides and are marketed as Clearfield® technology by BASF.

The incorporation of Group B resistance into crops enables post-emergent application of registered imidazolinone herbicide combinations to these crops that would damage non-Clearfield® lines. Clearfield® cultivars also have the advantage of tolerating Group B soil residues that might be present following application to the previous crop. See below under the heading *Soil activity* for more information on soil residues.

Photo 7: *Imi damage to conventional canola amongst imi tolerant lines. Herbicide sensitivity is exacerbated when plants are stressed due to cold, waterlogging or soil constraints because they are slower to metabolise the herbicide and exhibit damage symptoms and subsequent yield loss.*

Photo: Rohan Brill, NSW DPI

Table 3: *Differences in selectivity between Group B chemical classes.*

Herbicide	Selective in some grass crops	Selective in some dicot crops	Non-selective (soil-applied pre-emergent)
Imidazolinones	Clearfield® only	Clearfield® canola Imazethapyr (faba beans, mungbeans, field peas, peanuts, soybeans, lucerne)	Imazapyr (higher rates)
Sulfonylureas	Azimsulfuron (rice) Chlorsulfuron Ethoxysulfuron (sugarcane) Iodosulfuron Mesosulfuron Metsulfuron Sulfosulfuron	Rimsulfuron (tomatoes) Trifloxysulfuron (cotton)	Sulfometuron Tribenuron (fallow)
Sulfonamides	Florasulam Flumetsulam Metosulam (e.g. oats) Pyroxsulam	Flumetsulam (chickpeas, field peas, lentil) Metosulam (lupins)	

2B.6 Soil activity

Group B herbicides are soil-active because they are not strongly adsorbed to soil particles and have moderate water solubility, making them readily absorbed by plant roots.

2B.6.1 Imidazolinones

Imidazolinones are generally weakly bound to the soil but adsorption increases as organic matter and clay content increase. Adsorption increases as soil pH drops below 6.5. Persistence increases with declining pH.

Breakdown occurs through microbial degradation and low levels of photolysis on the soil surface.

Photo 8: *Non-Clearfield wheat sprayed with imi technology.*

Photo: David Pfeiffer

2B.6.2 Sulfonylureas

Sulfonylureas have low adsorption to clay and high adsorption to soil organic matter.

Non-microbial hydrolysis is high at pH <6.5 but degradation rates are slow at pH 7.5–8.0. Therefore, persistence increases with increasing soil pH.

Degradation rates increase with increasing temperature and soil moisture. Microbial degradation is slow, but varies between herbicides. For example, tribenuron-methyl has higher levels of microbial breakdown than metsulfuron, so the former has a shorter plant-back period.

Photo 9: *Ally residue effects on chickpeas.*

Photo: Kevin Moore, NSW DPI

Sulfonamides are weakly bound to soils. Soil adsorption increases at lower pH.

Primary mode of breakdown in the soil is microbial; therefore, rates are determined by temperature and available soil moisture.

Photo 10: *Eclipse damage on wheat.*

Photo: Harm van Rees

MORE INFORMATION

See the GRDC Spray Application GrowNote

https://grdc.com.au/Resources/GrowNotes-technical/Spray-Application-Manual

2B.7 Effect of environmental conditions on activity

2B.7.1 Light

High light conditions can thicken the cuticle of a weed, which will increase the length of the aqueous absorption route, thus reducing rates and potentially total absorption by Group B herbicides.

Group B herbicides are rapidly decomposed by photolysis in water, reducing environmental hazards, but they experience low levels of photolysis on the soil surface.

Decreasing light intensity, such as occurs in autumn, increases the ratio of shoots to rhizomes in perennial species, which leads to better control through better herbicide interception and more herbicide translocating to the root system. There is also an increase in the amount of starches and sugars moving into roots and storage organs, which in turn increases the transport of phloem-mobile Group B herbicides.

2B.7.2 Temperature

As temperature increases, the rate of uptake of herbicide increases provided respiration and photosynthesis are not limited by the conditions. However, the total amount of herbicide absorbed does not change. High temperatures and low available soil moisture reduce herbicide translocation through the shutdown of transpiration.

However, higher temperatures with lower humidity speed the drying of spray droplets on the leaf, thus reducing time available for absorption. This effect can be reduced by the type of adjuvant used and by maintaining the applied herbicide rate.

Optimum temperatures for photosynthesis and respiration are determined by whether the plants use C3 or C4 photosynthesis. C3 plants grow best at temperatures <30°C, whereas C4 plants can actively grow at temperatures up to 35°C and at higher light intensities.

Frost and cold weather with prolonged low light (cloud) will cause increased levels of crop damage. Low soil temperatures have been found to worsen sulfonylurea damage to cereal crops. Increased crop damage results from lower production of P450 enzymes due to reduced crop growth, and therefore, the herbicide is deactivated more slowly within the crop plant.

A range of research has shown that Group B herbicides are highly efficacious at temperatures of 15°–25°C; however, this will vary between the herbicides. Some research has shown that control of wild radish (*R. raphanistrum*) with flumetsulam increased by 7.5 times when temperature increased from 13°C to 20°C. However, metosulam control increased by only <2% over a similar temperature range.

2B.7.3 Humidity

The main effect of humidity with Group B herbicides is that weeds will likely be actively growing and will quickly translocate the herbicide to the meristems. This assumes adequate soil moisture. High humidity and low soil moisture will slow transpiration and, therefore, photosynthesis and growth.

High humidity increases the rate of herbicide absorption by maintaining a hydrated leaf cuticle.

Plants growing under high humidity also have thinner cuticles and are generally easier to control because of quicker uptake of herbicide.

2B.7.4 Soil moisture stress

Stressed plants have thicker cuticles, which will increase the length of the aqueous path accessed by Group B herbicides. These additional waxes or hairs can increase herbicide runoff and droplet bounce, reducing herbicide coverage.

Moisture stress will reduce translocation of the herbicide and reduce herbicide efficacy. Addition of certain adjuvants can assist herbicide absorption into the plant; however, if the plant is not actively growing, translocation and efficacy will be limited.

Research has shown that absorption of imazethapyr by common ragweed (*Ambrosia artemisiifolia*) under moisture stress was reduced by 10%, whereas translocation was unaffected. In the same experiment, humidity of 65–85% had no effect on absorption and translocation.

2B.7.5 Rain

Group B herbicides are rain-fast for 2–4 hours; however, because of their soil activity, weed control from herbicides such as chlorsulfuron has been found less affected by rain shortly after application.

Weeds exposed to multiple days of rain have been found to modify cuticular waxes and improve herbicide absorption.

Dew or light rain soon after application has been known to increase crop damage because it runs herbicide into the leaf axils, increasing the quantity of herbicide absorbed, which overwhelms the enzymes responsible for metabolising the herbicide before it reaches the meristem.

MORE INFORMATION

See the comprehensive GRDC Spray Application GrowNote for more information. https://grdc.com.au/Resources/GrowNotes-technical/Spray-Application-Manual

See the GRDC Adjuvants Booklet https://grdc.com.au/resources-and-publications/all-publications/publications/2015/04/adjuvants-booklet

2B.8 Spray application

Group B herbicides are well translocated within the plant, so spray coverage appears less critical than with contact herbicides. The spray target should be at least 8% coverage.

Label recommendations vary from a minimum application volume of 50 litres per hectare (L/ha) to 100–150 L/ha. Some imidazolinones have a minimum application volume of 70 L/ha.

Spray quality on labels generally recommends medium to coarse.

2B.8.1 Adjuvants

Sulfonylureas and sulfonamides are generally formulated as dry flowable products. These contain a surfactant to improve droplet retention.

Imidazolinones are produced as either soluble aqueous concentrates (e.g. Intervix®) or water-dispersible granules (e.g. Spinnaker® 700 WDG).

All Group B herbicides are recommended to be applied with an adjuvant, except Londax® and Arsenal® Xpress.

Read the label for recommended use of adjuvants.

2B.8.2 Water quality

Temperature

No data are available on the effect of low spray solution temperatures on efficacy.

pH

The effect of the pH of a spray solution is one of the most widely misunderstood concepts in spray application. Do not leave spray premixed overnight. Higher pH water is thought to improve slightly the efficacy of sulfonylurea herbicides.

Hardness

Despite Group B herbicides being weak acids, no evidence of the effect of hard water for spraying is available.

Turbidity

Muddy and water with low levels of algae pose a filter and nozzle blockage risk.

2B.9 Further reading

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Nalewaja JD, Woznica Z (1985) Environment and chlorsulfuron phytotoxicity. *Weed Science* 33, 395–399.

Shaner DL (2014) 'Herbicide handbook.' (Weed Science Society of America: Lawrence, KS, USA)

Somervaille A, Betts G, Gordon B, Green V, Burgis M, Henderson R (2012) 'Adjuvants—Oils, surfactants and other additives for farm chemicals.’ 2nd edn (GRDC: Kingston, ACT)

Herbicide Group C modes of action

The Group C Mode of Action (MoA) herbicides inhibit photosynthesis by blocking the action of photosystem II, through blocking the transfer of high-energy electrons needed by the plant to convert water and carbon dioxide to oxygen gas and sugars.

Group C herbicides are divided into three groups under the global Herbicide Resistance Action Committee (HRAC) and Weed Science Society of America (WSSA) systems, according to whether they block photosystem II at site A, B, or at site A with a different binding behaviour. Often there is no cross-resistance from one class to another, hence the three classifications. They are also classified as Groups C1, C2 and C3 by HRAC and Groups 5, 6 and 7 by WSSA (http://hrac.tsstaging.com/tools/classification-lookup).

There are nine chemical classes within the Group C MoA as shown in Table 1. These classes are different types of chemicals; however, they affect the same biochemical pathways in the plant.

Photo 1: *The effects of atrazine on mungbeans*

DPI&F

Table 1: *Herbicides included in Group C.*

Chemical class	Active ingredient	Product examples
Amides	Propanil	Stam®
Benzothiadiazinones	Bentazone	Basagran®, Basagran® M60 (PM)
Nitriles	Bromoxynil	Buctril® MA (PM), Eliminar C™ (PM), Flight® (PM), Jaguar® (PM), Triathlon® (PM), Velocity® (PM)
	Ioxynil	Actril® DS (PM), Totril®
Phenylcarbamates	Phenmedipham	Betanal®
Pyridazinones	Chloridazon	Pyramin®
Triazines	Ametryn	Amigan® (PM), Gesapax Combi® (PM), Krismat® (PM)
	Atrazine	Gesapax Combi® (PM), Gesaprim®, Primextra Gold® (PM)
	Cyanazine	Bladex®
	Prometryn	Cotogard® (PM), Gesagard®
	Propazine	No registered products
	Simazine	Gesatop®
	Terbuthylazine	Terbyne®
	Terbutryn	Agtryne® MA (PM), Amigan® (PM), Igran®
Triazinones	Hexazinone	Bobcat® i-Maxx (PM), Velpar® K4™ (PM), Velpar® L
	Metribuzin	Aptitude® (PM), Sencor®
Uracils	Bromacil	Hyvar®, Krovar® (PM)
	Terbacil	Eucmix® PrePlant (PM), Sinbar®
Ureas	Diuron	Krovar® (PM), Velpar® K4 (PM)
	Fluometuron	Cotogard® (PM), Cotoran®
	Linuron	Afalon®
	Methabenzthiazuron	Tribunil®
	Siduron	Tupersan®
	Tebuthiuron	Graslan™

PM, Product contains more than one active constituent; some products listed contain two active ingredients from one chemical class.

Source: http://www.croplife.org.au/resistance-strategy/herbicide-mode-of-action-groups/

The Group C herbicides are some of the oldest synthetic herbicides, with atrazine first commercialised in 1957.

Group C herbicides are used on a large scale worldwide. They are used as pre- and post-emergent herbicides in a wide range of crops as well as for fallow and non-agricultural weed control.

2C.1 Mode of action and biochemical pathways

Group C herbicides inhibit photosynthesis by binding to the plastoquinone (QB) binding niche on the D1 proteins of the photosystem II complex in the chloroplast thylakoid membranes. Herbicide binding at this location blocks electron transport from QA to QB and stops carbon dioxide fixation and the production of ATP and NADPH2. These are needed for plant growth. Photosynthesis is effectively stopped; however, plant death occurs by a number of processes.

The inability to readily oxidise QA promotes the formation of triplet-state chlorophyll, which interacts with oxygen to form singlet oxygen. Both triplet chlorophyll and singlet oxygen can extract hydrogen from unsaturated lipids, producing a lipid radical and initiating a chain reaction of lipid peroxidation. Lipids and proteins are attacked and oxidised, resulting in loss of chlorophyll and carotenoids and in leaky membranes that dry and disintegrate cells.

Some compounds in this group may in inhibit carotenoid synthesis (e.g. fluometuron) or synthesis of anthocyanin, RNA and proteins as well as causing disruption of the plasmalemma (e.g. propanil).

These herbicides require sunlight to work effectively. The more sunlight available the faster the symptoms develop.

2C.2 Absorption into the plant

Most Group C herbicides have a moderate level of water solubility (Table 2). Some are also weak acids. This means that they are absorbed through the aqueous route of the cuticle and through the roots.

Table 2: *Environmental characteristics of Group C herbicides.*

Group class	Active ingredient	Example trade name	Water solubility (mg/L)	Log K_{ow}	Soil persistence (half life @ 20°C) (days)	Soil mobility (K_{oc}/K_{foc})	Volatility (Henry's Law constant, 25°C)
Amides	Propanil	Stam®	95	2.29	0.4	152, moderate	Non-volatile
Benzothiadiazinones	Bentazone	Basagran®	7112	–0.46	7.5	55, mobile	Non-volatile
Nitriles	Bromoxynil	Bronco® 400	0.05	6.2	8	24,739, non	Non-volatile
Triazines	Atrazine	Gesaprim®	35	2.7	29	100, moderate	Non-volatile
	Prometryn	Cotagard®	33	3.34	41	400, moderate	Non-volatile
	Simazine	Gesatop®	5	2.3	90	130, moderate	Non-volatile
	Terbuthylazine	Terbyne®	7	3.4	23	231, moderate	Non-volatile
	Terbutryn	Igran®	25	3.66	52	2432, slight	Non-volatile
Triazinones	Hexazinone	Velpar®	33,000	1.17	60	54, mobile	Non-volatile
	Metribuzin	Sencor®	1165	1.65	19	38, mobile	Non-volatile
Uracils	Bromacil	Hyvar®	815	1.18	60	32, mobile	Non-volatile
	Terbacil	Sinbar®	710	1.89	120	55, mobile	Non-volatile
Ureas	Diuron	Diurex®	36	2.87	89	813, slight	Non-volatile
	Fluometuron	Cotoran®	111	2.28	90	67, mobile	Non-volatile
	Linuron	Afalon®	64	3	48	843, slight	Non-volatile
	Methabenzthiazuron	Tribunil®	60	2.64	.35	527, slight	Non-volatile

Log K_{ow}, ratio of herbicide that is soluble in octanol (organic solvent) v. water; it is a good indicator of the lipophilic or hydrophilic nature of a herbicide; the larger the log K_{ow} value the more lipophilic the herbicide; herbicides with values between –1 and 1 should move in the phloem following foliar application. K_{oc}/K_{foc}: >1000, binds strongly to soil; <500, move in water. Solubility will vary with temperature and to a lesser degree pH.

Source: Pesticides Properties Database: http://sitem.herts.ac.uk/aeru/ppdb/en/index.htm

2C.3 Translocation within the plant

Once inside the plant, Group C herbicides move almost exclusively within the xylem and have limited downward movement in the phloem. Although these herbicides are readily absorbed by the leaves, they accumulate on the margins of the leaf as they are moved there within the xylem. This is where the first symptoms appear.

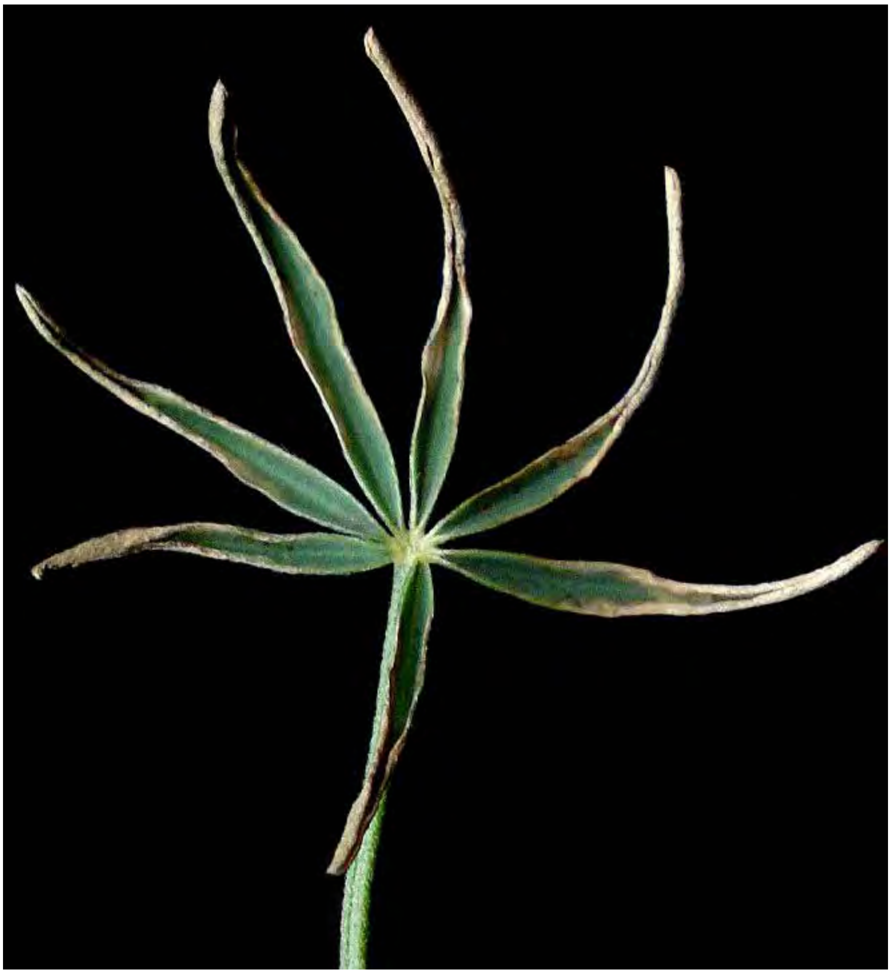

Photo 2: *Albus lupin with leaf margin affected by a Group C herbicide.*

Photo: DAFWA

2C.4 Symptoms

Symptoms begin with interveinal yellowing of the leaves and yellowing of the leaf margins. This yellowing spreads and turns to necrosis or browning. Older leaves are usually more affected than new growth.

With herbicides such as bromoxynil there tends to be a general yellowing of the leaves followed by necrosis. Bromoxynil essentially acts as a knockdown/contact herbicide.

VIDEO

Ohio State University Weed Science time lapse of the effect of foliar applied atrazine on waterhemp: https://youtu.be/wf1SsO_5x9A?list=PLrQLElJHkjuh65RjQZ8nWDBh0Da_MekB0

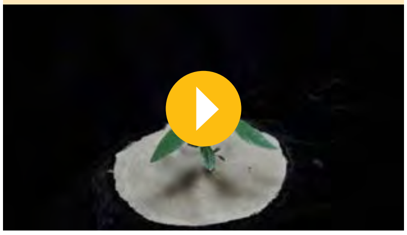

Photo 3: *Atrazine damage on a sorghum plant.*

Photo: Andrew Storrie, Agronomo

Photo 4: *Older leaves of canola showing the effects of Metribuzin.*

Photo: Harm van Rees

Photo 5: *Atrazine damage in sunflowers.*

Photo: NSW DPI

Photo 6: *Mecrosis on a soybean leaf from Cotoguard (prometryn + fluometuron).*

Photo: DPI&F


2015/06/25

Photo 7: *Metribuzin in barley.*

Photo: David Pfeiffer

2C.4.1 Timeframe for symptoms and plant death

Rate of development of symptoms and subsequent damage and death depend on the plant species, herbicide dose, age and size of plant, and rate of plant growth. Death occurs from as early as two weeks to around four–six weeks post-application.

- With foliar applications, interveinal chlorosis can begin within 2 days with foliar necrosis in 3–6 days.
- Symptom development in soil-absorbed herbicides is often slower because the herbicides need to be moved via the xylem to the leaves. This is strongly related to rate of plant growth and availability of soil moisture. If seeds germinate in the band of herbicide, they absorb herbicide as the seedling grows, and need at least two true leaves to accumulate a lethal dose.

2C.5 Crop selectivity

Selectivity within Group C herbicides is based on differential herbicide application rates and pathways of herbicide metabolism in the crops and weeds (Table 3). Species selectivity is conferred by rapid herbicide metabolism to non-toxic compounds by the crop but not the weed. Because of their poor phloem translocation, they are effectively burn-down herbicides when applied as a post-emergent treatment.

Selectivity of many herbicides is rate-dependent; they are non-selective at high application rates and selective at lower application rates. Diuron is an excellent example and is used as a selective post-emergent herbicide in winter cereal crops at low rates but is used for total vegetation control at high rates.

Selectivity of triazines occurs by several different processes. Truly tolerant species such as maize and sorghum metabolise triazines by a rapid enzymic process called glutathione conjugation, whereas partly tolerant species such as field peas (and wheat) use a slower N-dealkylation degradation. Some species have a degree of tolerance because their roots do not absorb the chemicals efficiently. If they also develop deep root systems rapidly, they will outgrow any herbicide damage from triazines. This is thought to be the main mechanism for tolerance in lupins. If the lupin taproot has been damaged by root disease, the plant is forced to survive on secondary roots growing in the surface soil. Consequently, the roots absorb more herbicide than normal and the lupin plant exhibits symptoms of triazine damage.

Photo 8: *Triazine damage to a lupin plant. Placement selectivity enables triazines to be used to control annual weeds near established trees. Very little of the surface-applied herbicide is taken up by the tree roots while annual weeds are controlled. However, heavy rainfall can move the herbicide into the root-zone of the trees. This causes increased herbicide absorption, which leads to tree damage and sometimes death.*

Photo: Tom De Matia, Delta Agribusiness

Bentazone is rapidly metabolised in tolerant species to form glucosyl conjugates.

The uracil herbicides bromacil and terbacil are not metabolised within the plant and are largely non-selective. They are used for total vegetation control. Selectivity of bromacil in orange trees is due to the low levels of root absorption and compartmentalisation of herbicide absorbed within the roots.

Selectivity of bromoxynil is due to a number of factors including higher levels of spray retention and increased absorption by broadleaf species, less contact with cereal growing points, and differences in the rate of metabolism. Selectivity of bromoxynil decreases at temperatures ≥20°C, leading to damage in otherwise tolerant species.

Table 3: *Differences in efficacy between Group C chemical classes*

Group C class	Herbicide example	Crops	Weeds
Amides	Propanil	Rice	Post-emergent control of barnyard grass
Benzothiadiazinones	Bentazone	Summer pulses	Post-emergent control of broadleaf weeds
Nitriles	Bromoxynil	Winter cereals, grain sorghum, linseed, clover, lucerne, turf	Post-emergent control of broadleaf weeds
Triazines	Atrazine	Triazine-tolerant canola, *Pinus* spp., *Eucalyptus* spp., grass pastures, lucerne, lupins, maize, sorghum, millet, sugarcane	Pre- and post-emergent. Range of grass and broadleaf species
Triazinones	Metribuzin	Barley, oats, wheat (limited), chickpeas, faba beans, lentils, lupins, field peas, pigeon peas, potatoes, soybeans, tomatoes	Range of broadleaf weeds and suppression of some annual grasses
Uracils	Bromacil	Total vegetation control and some crops	All seedlings and annual weeds
Ureas	Diuron	Asparagus, bananas, cotton (banded), established lucerne, winter pulses, sugarcane, wheat, irrigation channels	Wide range of annual broadleaf and grass weeds

Group C herbicides are often used in tank mixes to broaden the number of species controlled and to improve control on larger weeds. For example, the phenoxy MCPA is often combined with diuron to broaden the control spectrum as an early post-emergent treatment in wheat. Bromoxynil is also premixed with MCPA to broaden the control spectrum and improve herbicide robustness.

For total vegetation control, Group C herbicides are best applied to bare ground or small weeds only, because of their limited translocation in the phloem.

There is also some synergy between some Group C herbicides and Group I or H when used in tank mixes. That is, the effect of these tank mixes is greater than the additive effects.

Some research has also shown that adding either metribuzin or diuron to paraquat improves the control of glyphosate- and glufosinate-resistant maize up to the V4 stage compared with paraquat alone.

MORE INFORMATION

See the comprehensive GRDC Spray Application GrowNote for more information.

https://grdc.com.au/Resources/GrowNotes-technical/Spray-Application-Manual

2C.6 Effect of environmental conditions on activity

Group C herbicides have moderate water solubility and some are weak acids, so they enter the plants via the aqueous pathway. Absorption and translocation of post-emergent applications will be affected by temperature, relative humidity and moisture stress.

Soil (pre-emergent) applications will be greatly affected by available soil moisture. The herbicide must be dissolved in the soil-water matrix to be absorbed by the roots, and uptake and transport in the xylem is dependent upon sufficient soil water to support actively growing plants.

Photo 9: *Simazine and Balance damage exacerbated by frost.*

Photo: Kevin Moore, NSW DPI

Photo 10: *Metribuzin damage in lupins exacerbated by frost within 24 hours of application.*

Photo: David Pfeiffer

2C.6.1 Light

High light conditions can thicken the cuticle of a weed, which will in turn reduce the uptake of water-soluble formulations.

Bentazone is more rapidly absorbed and translocated under conditions of high than low light intensity, whereas other herbicides such as ioxynil and bromoxynil are more active at lower light intensities. Ioxynil and bromoxynil act as post-emergent contact herbicides and low light conditions might inhibit the plant's ability to regrow after spraying. On the other hand, the efficacy of soil-applied group C herbicides increases with light intensity.

2C.6.2 Temperature

As temperature increases, the rate of uptake of foliar-applied herbicide increases provided respiration and photosynthesis are not limited by the conditions. However, the total amount of herbicide absorbed does not change. High temperatures and low available soil moisture reduce herbicide translocation through the shutdown of transpiration. Performance of foliar-applied bromoxynil and ioxynil increases with increasing temperature.

2C.6.3 Humidity

Plants growing in conditions of higher humidity have less epidermal wax on the leaf surface than plants growing in low humidity. High humidity hydrates the cuticle, allowing a continuous aqueous path to the epidermis for these water-soluble herbicides.

2C.6.4 Soil moisture stress

Moisture-stressed plants have thicker cuticles that will slow the absorption of foliar-applied Group C herbicides. Addition of certain adjuvants can assist herbicide absorption into the plant.

Low soil-moisture conditions reduce root absorption and translocation of soil-applied Group C herbicides.

In addition, photosynthesis will be limited, which will slow the activity of the herbicide, reducing levels of control.

2C.6.5 Rainfall

The rain-fast period for foliar application of Group C herbicides varies from three to eight hours.

For pre-emergent applications, labels can warn not to apply the herbicide if significant rain is pending. Heavy rains following application can move the herbicide into the root-zone and increase crop damage. The risk will vary with the water solubility of the herbicide. For example, simazine is far less water-soluble than atrazine, so atrazine will present a higher risk of crop damage. Potential damage will be higher on light-textured soils.

2C.7 Spray application

Foliar applied of Group C herbicides require very good coverage because these herbicides are effectively contact herbicides with little downward translocation. Newer labels are recommending that they be applied as a coarse spray quality; therefore, application volumes need to be kept above 70 litres per hectare to ensure adequate coverage.

Target coverage should be towards 15% as measured with water-sensitive paper.

Soil-applied herbicides need even coverage; however, they can be applied in a coarse to extremely coarse spray quality. If tank-mixed with a knockdown herbicide, they should be applied in the relevant spray quality for that knockdown herbicide.

2C.7.1 Adjuvants

Read the label for recommended use of adjuvants. Foliar applications of Group C herbicides often require an adjuvant to improve retention and absorption of the herbicide. Adjuvants can vary from a non-ionic surfactant to a spray oil.

MORE INFORMATION

See the comprehensive GRDC Spray Application GrowNote for more information.
https://grdc.com.au/Resources/GrowNotes-technical/Spray-Application-Manual

See the GRDC Adjuvants Booklet
https://grdc.com.au/resources-and-publications/all-publications/publications/2015/04/adjuvants-booklet

Soil-applied Group C herbicides do not require an adjuvant.

2C.7.2 Water quality

pH

Spray acidity or alkalinity is largely irrelevant with these herbicides as long as they are in the normal range of pH 5–7.5.

Hardness

Because these herbicides can be weak acids, water hardness can be important. The presence of calcium and magnesium ions should be treated with ammonium sulfate.

Salinity

Diuron can be affected by high salinity levels, as can a tank mix of diuron plus MCPA.

Turbidity

Group C herbicides are generally not affected by the presence of clay and particulate matter in the spray solution; however, water of this quality should be treated to reduce blocking of filters and nozzles.

2C.8 Further reading

Caseley JC (1987) Effects of weather on herbicide activity. In ‘Eighth Australian Weeds Conference’. pp. 386–394.

Gregory JS, Robert EN, Peter HS (2013) The effect of time of day on the activity of postemergence soybean herbicides. *Weed Technology* 27, 690–695.

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Herbicide Group D modes of action

The Group D Mode of Action (MoA) herbicides inhibit cell division by blocking the production of protein ropes (microtubule fibres) that separate chromosome duplicates during cell division.

Group D herbicides are also classified as Groups K1 by the global Herbicide Resistance Action Committee (HRAC) and Group 3 by the Weed Science Society of America (WSSA) (http://hrac.tsstaging.com/tools/classification-lookup).

There are four chemical classes within the Group D MoA as shown in Table 1. These classes are different types of chemicals; however, they affect the same biochemical pathways in the plant.

Table 1: *Herbicides included in Group D.*

Chemical class	Active ingredient	Product examples
Benzamide	Propyzamide	Kerb™
Benzoic acid	Chlorthal-dimethyl	Dacthal®
Dinitroanilines	Oryzalin	Surflan®
	Pendimethalin	Stomp®
	Trifluralin	Treflan™
Pyridines	Dithiopyr	Dimension®

Source: http://www.croplife.org.au/resistance-strategy/herbicide-mode-of-action-groups/

The Group D herbicides are some of the oldest synthetic herbicides, first commercialised in 1961.

Group D herbicides are mostly used for pre-emergent control of a range of grass and broadleaf weeds in a wide range of field crops, horticulture, pastures and turf. Herbicides such as propyzamide have limited post-emergent activity on small weeds.

2D.1 Mode of action and biochemical pathways

Group D herbicides bind to tubulin, the major microtubule protein. This tubulin–herbicide complex stops the assembly of microtubules but does not prevent their deconstruction. This leads to a loss of microtubule structure and function, stopping formation of the spindle apparatus during cell division and hence preventing the alignment and separation of chromosomes to be distributed between the 'daughter' cells. Because microtubules also function in the formation of cell walls, this also stops cell division. This is expressed as the swelling of root tips as cells in this region neither divide nor elongate.

VIDEO

Plant mitosis and the role of spindles and the cell plate: https://www.youtube.com/watch?v=4govZdjEBrs&feature=youtu.be

2D.2 Absorption into the plant

Group D herbicides are primarily absorbed by the emerging plant shoots (grass coleoptile, hypocotyl or epicotyls of dicots) or secondarily by the seedling roots. Some absorption of dinitroaniline vapour may occur. Trifluralin binds tightly to the lipid components of cell membranes.

Photo 1: *Wheat seedlings stunted and struggling to emerge from the coleoptile due to trifluralin.*

Photo: Harm van Rees

2D.3 Translocation within the plant

There is little translocation of Group D herbicides within the plant owing to their strong lipophilic nature (Table 2).

Established plants readily absorb trifluralin into the roots but upward movement in the plant is limited. The highly lipophilic nature of trifluralin means that it is rapidly absorbed into membranes and other parts of root tissues, limiting its translocation to the shoots. Trifluralin will have little effect when applied to the foliage of a plant.

Propyzamide is readily absorbed into the roots and distributed throughout the plant by upward translocation in the apoplast (includes the xylem). It also has foliar activity on seedlings of some weed species. Translocation of foliar-applied propyzamide is minimal.

Table 2: *Environmental characteristics of Group D herbicides.*

Group class	Active ingredient	Example trade name	Water solubility (mg/L)	Log K_{ow}	Soil persistence (half-life @ 20°C) (days)	Soil mobility (K_{oc}/K_{foc})	Volatility (Henry's Law constant, 25°C)
Benzamide	Propyzamide	Kerb™	9	3.3	233	840, slightly	Non-volatile
Benzoic acid	Chlorthal-dimethyl	Dacthal®	0.21	4.3	47	2963,slightly	Moderately volatile
Dinitroanilines	Oryzalin	Surflan®	1.13	3.7	98	949, slightly	Non-volatile
	Pendimethalin	Stomp®	0.3	5.4	101	17,490, non	Non-volatile
	Trifluralin	Treflan™	0.2	5.3	170	15,800, non	Volatile
Pyridines	Dithiopyr	Dimension®	1.4	5.9	39	801, slightly	Non-volatile

Log K_{ow}, ratio of herbicide that is soluble in octanol (organic solvent) v. water; it is a good indicator of the lipophilic or hydrophilic nature of a herbicide; the larger the log K_{ow} value the more lipophilic the herbicide; herbicides with values between –1 and 1 should move in the phloem following foliar application. K_{oc}/K_{foc}: >1000, binds strongly to soil; <500, moves in water. Solubility will vary with temperature and to a lesser degree pH.

Source: Pesticides Properties Database, http://sitem.herts.ac.uk/aeru/ppdb/en/index.htm

2D.4 Symptoms

Susceptible small-seeded annual grasses and broadleaf weeds fail to emerge; however, seed germination is not inhibited. Established plants have stunted root systems with deformed and swollen root tips. Grass stems may be purple at the base. The base of grass stems may also become swollen. Shoots may be deformed and brittle.

Photo 2: *Wheat seedlings with shortened coleoptiles and stunted root systems from 2 L trifluralin/Ha.*

Photo: David Pfeiffer

Photo 3: *Propyzamide damage in TT canola.*

Photo: David Pfeiffer

Photo 4: *Shortened coleoptiles in wheat leading to the first true leaf to struggle with emergence. Leaves can look consortia-like from trifluralin.*

Photo: Bill Long

Photo 5: *Ryegrass roots severely stunted from propyzamide.*

Photo: Andrew Storrie, Agronomo

Photo 6: *Propyzamide affecting oat plants.*

Photo: Andrew Storrie, Agronomo

2D.4.1 Timeframe for symptoms and plant death

Seeds that germinate within the soil–herbicide layer and absorb the herbicide do not emerge as long as there is sufficient soil moisture to activate the herbicide.

Plants that germinate above the herbicide layer can establish but have their root systems stunted. These plants can grow leaves and shoots until they undergo moisture stress in spring, then they die.

Plants germinating below the herbicide layer or managing to germinate in the herbicide layer with insufficient moisture to activate the herbicide can also establish and grow as long as their meristems grow beyond the treated layer. This can take between two weeks and several months depending on growing conditions and species.

2D.5 Crop selectivity

Selectivity in Group D herbicides is not based on metabolism but it is based on:

- almost no translocation within the plant (due to a highly lipophilic nature)
- depth of soil incorporation
- the differing position of the meristematic region of weed and crop.

2D.5.1 Grass weeds and cereal crops

Primary roots and the coleoptile node are the active sites in cereal crops and grass weeds. The position of the primary root is the same in crops and grass weeds, but the position of the coleoptile node will vary. For example, wild oats push the coleoptile upward (have a mesocotyl), which pushes the Group D-sensitive coleoptile node into the herbicide-treated soil. Wheat and barley do not have a mesocotyl, so the coleoptile node remains below the herbicide-treated soil.

With the development of direct seeding of crops, the pattern of use for trifluralin has changed. The original use pattern consisted of a trifluralin rate of less than one litre per hectare (L/ha), which was then incorporated within four hours of application to the top 50 mm of soil. With direct planting techniques, the application rate is 1.5–3 L/ha, applied within 24 hours of planting. The higher herbicide rate is required if significant crop residues are present and to account for vapour losses before incorporation. To maintain crop safety, a tined machine is needed to push herbicide-treated soil away from the crop row. This has the disadvantage of removing the herbicide from the crop row, which allows weeds to germinate and establish.

Photo 7: *Trifluralin stripped from the plant rows allowing grass weeds to germinate in a canola crop.*

Photo: Penny Heuston

2D.5.2 Broadleaf weeds and crops

Selectivity between broadleaf crops and weeds is poorly understood; however, there is some evidence that plants that have seeds with high oil content somehow tolerate Group D herbicides. Another theory suggests less root uptake in certain broadleaf species.

Wireweed (*Polygonum aviculare*), tree hogweed (*P. bellardii*), poppies (*Papaver* spp.) and black bindweed (*Fallopia convolvulus*) are particularly sensitive to the dinitroaniline herbicides (Table 3).

Table 3: *Differences in efficacy between Group D chemical classes.*

Group D class	Herbicide example	Crops	Weeds
Benzamide	Propyzamide	Canola, legume pastures, oilseed poppies, lettuce, turf	Mostly pre-emergent control: annual ryegrass, barley grass, Canary grass, fescue, great brome, prairie grass, *Vulpia* spp., wild oats, winter grass Bent grass, blackberry, nightshade, chickweed, English couch, Paterson's curse, perennial ryegrass, seedling sorrel, seedling wireweed, Yorkshire fog grass
Benzoic acid	Chlorthal-dimethyl	Brassicas, green beans, field peas, garlic, onions, carrots, lettuce, potatoes, turnips; and for weed control in strawberries, cotton, lucerne, perennial grass crops, lawns and ornamentals	Pre-emergent control of a wide range of grass and broadleaf weeds Can apply over established turf
Dinitroanilines	Oryzalin	Fruit and nut orchards, vineyards, nursery stock, ornamental and amenity plantings	Pre-emergent control of wide range of grass and broadleaf weeds
	Pendimethalin	Barley, wheat, chickpeas, faba beans, field peas, lentils, lupins, safflower, soybeans, peanuts, navy beans, cow peas, mungbeans, pigeon peas, cotton, carrots, processing peas, onions, sugarcane, drill-sown rice, perennial crops plus others	Mainly pre-emergent control of a wide range of grass and broadleaf weeds Can apply over the top of eucalypts, pyrethrum, oil tea-tree, established lucerne, turf
	Trifluralin	Wheat, barley, triticale, canola, chickpeas, adzuki beans, cowpeas, lablab, mungbeans, borlotti beans, red kidney beans, faba beans, pigeon peas, lentils, navy beans, soybeans, vetch, cotton, sugarcane, linseed, field peas, peanuts, sunflowers, lupins, tobacco plus others	Pre-emergent control of wide range of grass and broadleaf weeds
Pyridines	Dithiopyr	Turf	Pre-emergent control of *Digitaria* spp., *Echinochloa* spp., *Eleusine indica*, *Stellaria media*

2D.6 Effect of environmental conditions on activity

The main environmental conditions affecting the activity of Group D herbicides are temperature and available soil moisture.

Several researchers in Australia and Europe have found that degradation of propyzamide accelerates with use. One team found that soil half-life declined from 31 days in previously untreated soil to 10 days on plots treated 14 times. This is thought to be due to increased microbial degradation. This effect will translate to shorter periods of effective weed control with propyzamide.

Overseas, propyzamide has been found in drinking water and its use is under review.

2D.6.1 Temperature

Warmer temperatures increase the rate of cell division and therefore the rate of plant deformation, because Group D herbicides affect cell division.

The rate of volatilisation of trifluralin and chlorthal-dimethyl from the soil surface increases with increasing temperature.

2D.6.2 Soil moisture

Adequate soil moisture in the herbicide layer is essential for absorption of the herbicides into the plant meristems. Dry soils tend to favour weeds to emerge through the herbicide layer. Trifluralin is thought to form a vapour in the presence of soil moisture, which is then absorbed into the plant meristem. Without adequate soil moisture, trifluralin remains tightly bound to the soil particles. Application of trifluralin to moist soils without incorporation leads to large herbicide losses via volatilisation.

2D.6.3 Rainfall

Most Group D herbicides are tightly bound to soil particles and organic matter. There is little leaching with Group D herbicides; however, there can be some incorporation of pendimethalin, oryzalin, propyzamide and chlorthal-dimethyl with 12–25 mm of rain or irrigation.

MORE INFORMATION

See the comprehensive GRDC Spray Application GrowNote for more information.
https://grdc.com.au/Resources/GrowNotes-technical/Spray-Application-Manual

See the GRDC Adjuvants Booklet
https://grdc.com.au/resources-and-publications/all-publications/publications/2015/04/adjuvants-booklet

2D.7 Spray application

Group D herbicides require even coverage of the soil because there is little movement once applied. Most labels recommend a minimum application volume of 70 L/ha, although label recommendations range from 50 to 200 L/ha. The greater the amount of crop residue present, the higher the application volumes recommended.

Although not mentioned on labels, the best penetration of standing stubble is achieved by application with the finer end of coarse spray quality. Droplets of this size have sufficient momentum to penetrate the canopy but not so much momentum (such as with extremely coarse droplets) that they ‘crash’ into the stubble and paint it with herbicide. If little crop residue is present, extremely coarse droplets can be used.

Target coverage should be towards 15% as measured with water-sensitive paper.

2D.7.1 Adjuvants

Read the label for recommended use of adjuvants. Generally, adjuvants are not required unless the Group D herbicides are being applied in a tank mix and the tank mix partner requires an adjuvant.

2D.7.2 Water quality

Group D herbicides are not sensitive to water quality.

2D.8 Further reading

Caseley JC (1987) Effects of weather on herbicide activity. In 'Eighth Australian Weeds Conference'. pp. 386–394.

Congreve M, Cameron J (2014) 'Soil behaviour of pre-emergent herbicides in Australian farming systems—reference manual for advisers.' (GRDC: Kingston, ACT)

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Hall L, Beckie H, Wolf TM (2009) 'How herbicides work. Biology to application.' (Government of Alberta, Alberta Agriculture and Rural Development: Edmonton, AB, Canada)

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Kudsk P, Kristensen JL (1992) Effect of environmental factors on herbicide performance. In 'Proceedings First International Weed Control Congress'. pp. 17–21.

Piper T, Stewart V (2005) 'Understanding herbicides.' (Department of Agriculture & Food WA: Perth, WA)

Shaner DL (2014) 'Herbicide handbook.' (Weed Science Society of America: Lawrence, KS, USA)

Somervaille A, Betts G, Gordon B, Green V, Burgis M, Henderson R (2012) 'Adjuvants—Oils, surfactants and other additives for farm chemicals.' 2nd edn (GRDC: Kingston, ACT)

Herbicide Group F modes of action

The Group F Mode of Action (MoA) herbicides inhibit carotenoid biosynthesis by blocking the phytoene desaturase enzyme. Symptoms include the bleaching of new growth.

Group F herbicides are also classified as Group 12 by the global Herbicide Resistance Action Committee (HRAC) and Group F1 by the Weed Science Society of America (WSSA) (http://hrac.tsstaging.com/tools/classification-lookup).

There are two chemical classes within the Group F MoA as shown in Table 1. These classes are different types of chemicals; however, they affect the same biochemical pathways in the plant.

Table 1: *Herbicides included in Group F.*

Chemical class	Active ingredient	Product examples
Pyridazinones	Norflurazon	Zoliar®
Pyridinecarboxamide	Diflufenican	Brodal®, Spearhead® (PM), Jaguar® (PM), Tigrex® (PM), Triathlon® (PM)
	Picolinafen	Sniper®, Eliminar™ C (PM), Flight® (PM), Paragon®

PM, Product contains more than one active constituent.

Source: http://www.croplife.org.au/resistance-strategy/herbicide-mode-of-action-groups/

Norflurazon was the first of the Group F herbicides and was commercialised in 1968, whereas diflufenican was commercialised in 1990.

Norflurazon is used as a pre-emergent herbicide in a wide range of field and horticultural crops for the control of grasses, sedges and broadleaf weeds. Diflufenican and picolinafen are used for post-emergent control of broadleaf weeds in pulses and legume pastures. When mixed with bromoxynil (Group C) or MCPA (Group I), they are used for broadleaf weed control in winter cereals.

2F.1 Mode of action and biochemical pathways

Group F herbicides block the production of carotenoids by inhibiting the enzyme phytoene desaturase.

Carotenoids play an important part in photosynthesis by capturing light energy and transferring it to the chlorophyll. Carotenoids also play three major protective roles in the photosynthetic apparatus. The first is to quench triplet chlorophyll molecules back to the ground state. The second is to quench singlet oxygen molecules back to the normal and non-destructive triplet state. The third is to moderate the photosystem reaction centres in very bright light.

If triplet chlorophyll is not moderated, it will produce reactive oxygen that destroys the photosynthetic apparatus within the thylakoid membrane. Destruction of chlorophyll leads to bleaching of the plant tissue.

Plants treated with Group F herbicides have lower levels of carotenoids; this allows the oxygen radicals to remove hydrogen from membrane fatty acids, producing a lipid radical. These lipid radicals interact with molecular oxygen to form peroxidised and other lipid radicals. This creates a self-sustaining chain reaction of lipid peroxidisation that destroys chlorophyll and membrane lipids. Proteins are also damaged. The destruction of integral membrane components leads to leaky membranes and rapid tissue desiccation.

Photo 1: *Bleaching of the plant tissue.on a radish plant from diflufenican.*

Photo: Penny Heuston

For detailed explanation, go to Plant and Soil Sciences e-Library: Inhibitors of carotenoid biosynthesis.

2F.2 Absorption into the plant

Group F herbicides are lipophilic and have low water solubility (Table 2). Pyridinecarboxamide herbicides are absorbed through the leaves of emerged plants and the roots and shoots of emerging seedlings. Diflufenican and picolinafen are absorbed through the leaves and have some soil residual activity. Absorption by susceptible species is thought to be faster than in tolerant species such as wheat. Group F herbicides are formulated as emulsifiable concentrates to aid mixing and foliar absorption.

Norflurazon is a soil-active pre-emergent herbicide and is absorbed into the roots by diffusion. It is a dry flowable formulation applied to bare soil or tank mixed with a knockdown herbicide.

Table 2: *Environmental characteristics of Group F herbicides.*

Group F class	Active ingredient	Example trade name	Water solubility (mg/L)	Log K_{ow}	Soil persistence (half-life @ 20°C) (days)	Soil mobility (K_{oc}/K_{foc})	Volatility (Henry's Law constant, 25°C)
Pyridazinones	Norflurazon	Zoliar®	34	2.45	225	700, moderate	Non-volatile
Pyridinecarboxamide	Diflufenican	Brodal®	0.05	4.2	315	1996, slight	Non-volatile
	Picolinafen	Sniper®	0.05	5.43	31	28,300, non-mobile	Non-volatile

Log K_{ow}, ratio of herbicide that is soluble in octanol (organic solvent) v. water; it is a good indicator of the lipophilic or hydrophilic nature of a herbicide; the larger the log K_{ow} value the more lipophilic the herbicide; herbicides with values between –1 and 1 should move in the phloem following foliar application. K_{oc}/K_{foc}: >1000, binds strongly to soil; <500, moves in water.

Source: Pesticides Properties Database, http://sitem.herts.ac.uk/aeru/ppdb/en/index.htm

2F.3 Translocation within the plant

There is limited translocation from the leaves to other parts of the plant. Root uptake and translocation is via the xylem.

Susceptible species also appear to have more rapid translocation within the plant.

2F.4 Symptoms

Symptoms on larger plants begin with bleaching of the new growth. This bleaching and yellowing spreads through the plant and turns to necrosis or browning.

Susceptible weeds germinate but show immediate chlorosis followed by irregular patches of white and/or mauve–pink discoloration. The chlorosis spreads within the aerial growth and the plants become necrotic and die.

Lentils and lupins often show transient yellow or white banding on the leaves.

Photo 2: *Chlorosis from diflufenican in barley.*

Photo: David Pfeiffer

Photo 3: *Brodal residues on TT canola causing purpling and bleaching.*

Photo: David Pfeiffer

Photo 4: *Zoliar (norflurazon) effects on wheat.*

Photo: Andrew Storrie

2F.4.1 Timeframe for symptoms and plant death

Rate of development of symptoms and subsequent damage and death depend on the plant species, herbicide dose, age and size of plant, and rate of plant growth. Symptoms begin about five–seven days post-application. Death occurs from as early as two weeks to four–eight weeks post-application.

2F.5 Crop selectivity

Selectivity appears to be a function of differential absorption and translocation between susceptible and tolerant species as well as size of plants when treated (i.e. effective dose received). In most instances, diflufenican and picolinafen are applied to pastures and crops once they have the emerged. Pasture legumes should have at least three trifoliate leaves and pulse crops must be well established (see label critical comments) before these herbicides are applied. See Table 3 for details of uses of Group F herbicides.

Norflurazon lacks crop selectivity as a post-emergent herbicide.

Diflufenican and picolinafen are tank-mixed with either a Group C or Group I herbicide, or both, or are available in formulations with Group C or Group I herbicides (e.g. Jaguar®, Tigrex®, Paragon®), to broaden the weed-control spectrum in winter cereals.

Photo 5: *Jaguar damage in wheat.*

Photo: David Pfeiffer

Table 3: *Differences in efficacy between Group F chemical classes.*

Group F class	Herbicide example	Crops	Weeds
Pyridazinones	Norflurazon	Asparagus, citrus, cotton, cotton fallow, grapes, nuts, pome fruit and stone fruit	Nutgrass (*Cyperus* spp.) and other grass and broadleaf weeds
Pyridinecarboxamide	Diflufenican	Clover-based pasture, lupins, field peas, lentils, oilseed poppy	*Brassica* weeds, prickly lettuce, pheasant's eye; suppression of a range of broadleaf weeds
	Picolinafen	Field peas, narrow-leafed lupins	Wild radish (*R. raphanistrum*), suppression of capeweed

MORE INFORMATION

See the comprehensive GRDC Spray Application GrowNote for more information.

https://grdc.com.au/Resources/GrowNotes-technical/Spray-Application-Manual

2F.6 Effect of environmental conditions on activity

Because Group F herbicides are poorly translocated, they act as contact herbicides when applied after weed emergence. Absorption of these herbicides via the roots is important for effective control, so available soil moisture is one of the critical factors in determining the efficacy of these herbicides.

2F.6.1 Light

These herbicides are used in winter on small weeds; therefore, light will have little effect except that sunny conditions will speed the development of symptoms.

2F.6.2 Temperature

As temperature increases, the rate of photosynthesis increases, and this speeds the production of radicals within the photosynthetic system. Frosts and cold stress will reduce the effectiveness of these herbicides.

2F.6.3 Humidity

Plants growing in higher humidity have less epidermal wax on the leaf surface than plants growing in low humidity. These conditions will increase the amount of foliar-applied herbicide entering the plant.

2F.6.4 Soil moisture stress

Moisture-stressed plants have thicker cuticles, which will slow the absorption of foliar-applied Group F herbicides. Addition of certain adjuvants can assist herbicide absorption into the plant.

Adequate moisture is required in the surface soil to enable root absorption of norflurazon, diflufenican and picolinafen. Drying of the surface soil will reduce the level of weed control when using these herbicides.

If crops are moisture-stressed, the level of damage from these herbicides will increase dramatically because plants will not be able to metabolise the herbicides before they affect photosynthesis.

2F.6.5 Rainfall

The rain-fast period for foliar application of group F herbicides is four hours.

MORE INFORMATION

See the GRDC Adjuvants Booklet https://grdc.com.au/resources-and-publications/all-publications/publications/2015/04/adjuvants-booklet

Rain within four hours of application could reduce foliar uptake; however, it is likely to improve root uptake as long as there is no major run-off or erosion.

2F.7 Spray application

Foliar-applied Group F herbicides require very good coverage, because these herbicides are effectively contact herbicides with little downward translocation. Labels recommend applying 50–100 litres per hectare but they do not mention spray quality.

Medium to coarse spray quality should be used, depending on the situation. Target coverage should be 10–15% as measured with water-sensitive paper.

If Group F herbicides are in a tank mix with a Group I herbicide, they must be applied as a coarse (or larger) spray quality.

Soil-applied herbicides require an even coverage; however, they can be applied in a coarse to extremely coarse spray quality. If tank-mixed with a knockdown herbicide, they should be applied in the relevant spray quality for that knockdown herbicide.

2F.7.1 Adjuvants

Adding adjuvants is generally not recommended. Read the label for recommended uses of adjuvants.

2F.7.2 Water quality

Water quality has little effect on Group F herbicides, provided it is within reasonable guidelines.

2F.8 Further reading

Caseley JC (1987) Effects of weather on herbicide activity. In 'Eighth Australian Weeds Conference'. pp. 386–394.

Kudsk P, Kristensen JL (1992) Effect of environmental factors on herbicide performance. In 'Proceedings First International Weed Control Congress'. pp. 17–21.

Piper T, Stewart V (2005) 'Understanding herbicides.' (Department of Agriculture & Food WA: Perth, WA)

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Somervaille A, Betts G, Gordon B, Green V, Burgis M, Henderson R (2012) 'Adjuvants—Oils, surfactants and other additives for farm chemicals.' 2nd edn (GRDC: Kingston, ACT)

Herbicide Group G modes of action

The Group G Mode of Action (MoA) herbicides are another group affecting photosynthesis. They inhibit protoporphyrinogen oxidase (PPO or protox), resulting in a loss of chlorophyll and carotenoids and in leaky membranes, which allow cells and cell organelles to dry and disintegrate rapidly.

Photo 1: *Peanuts showing a loss of chlorophyll and cells that have subsequently dried out from a Blazer (actiflurofen) application.*

Photo: DAF

There are six chemical classes within the Group G MoA as shown in Table 1. These classes are different types of chemicals; however, they affect the same biochemical pathways in the plant. They are also classified as Group E by the global Herbicide Resistance Action Committee (HRAC) and Group 14 by the Weed Science Society of America (WSSA) (http://hrac.tsstaging.com/tools/classification-lookup).

Table 1: *Herbicides included in Group G.*

Chemical class	Active ingredient	Product examples
Diphenyl ethers	Acifluorfen	Blazer®
	Oxyfluorfen	Goal™, Rout® (PM)
N-phenylphthalimides	Flumioxazin	Valor®
Oxadiazoles	Oxadiargyl	No registered products
	Oxadiazon	Ronstar®
Phenylpyrazoles	Pyraflufen	Ecopar®, Pyresta® (PM)
Pyrimidindiones	Butafenacil	Logran® B-Power® (PM)
	Saflufenacil	Sharpen®
Triazolinones	Carfentrazone	Hammer®, Affinity® Plus (PM), Aptitude® (PM), Broadway® (PM)

PM, Product contains more than one active constituent.

Source: http://www.croplife.org.au/resistance-strategy/herbicide-mode-of-action-groups/

Because of their rapid desiccation of plant tissues, some of these herbicides are commonly used as 'spikes' added at lower rates to other knockdown herbicides to speed 'brown-out'. Others can be used at higher rates as soil residual herbicides in plantations and horticulture.

Carfentrazone and acifluorfen are used as post-emergent herbicides in a range of crops to control broadleaf weeds. Carfentrazone is also formulated for application to water bodies to control aquatic weeds.

2G.1 Mode of action and biochemical pathways

Group G herbicides block PPO, which is an enzyme involved in biosynthesis of chlorophyll and heme (needed for electron transfer chains), catalysing the oxidation of protoporphyrinogen to protoporphyrin IX (Figure 1). This leads to the accumulation of protoporphyrinogen IX, the first light-absorbing chlorophyll precursor. This accumulated precursor, in the presence of sunlight, reacts with molecular oxygen to form oxygen radicals, which in turn produce lipid radicals, initiating a chain reaction of lipid oxidisation. Lipids and proteins are attacked and oxidised, resulting in loss of chlorophyll and carotenoids and in leaky membranes. The leaky membranes mean that cells and cell organelles rapidly dry and disintegrate.

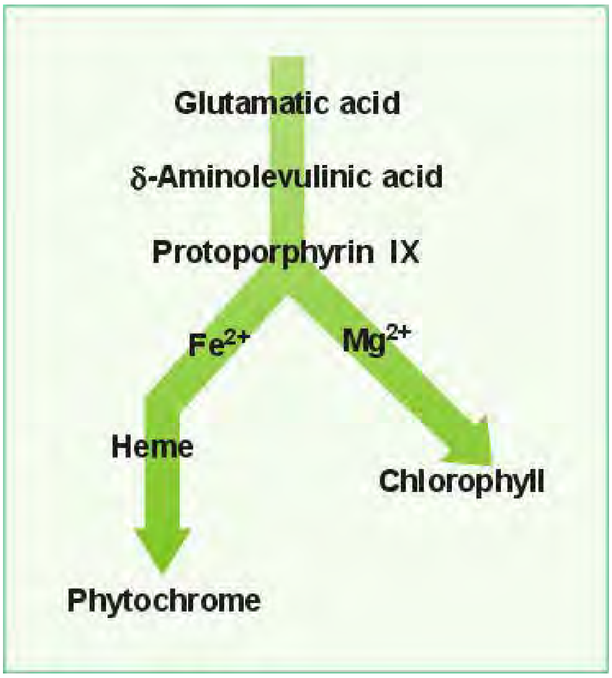

Figure 1: *Biosynthesis pathway affected by Group G herbicides.*

2G.2 Absorption into the plant

Group G herbicides are rapidly absorbed by the foliage of plants, whereas root absorption is variable. Oxyfluorfen is poorly absorbed via the roots, and saflufenacil is well absorbed.

Soil-applied herbicide is absorbed by the shoots of emerging seedlings, with some uptake via the roots depending on the herbicide.

2G.3 Translocation within the plant

Group G herbicides are largely considered contact herbicides, in that transport is limited owing to the rapid desiccation of plant foliage, although some species are well controlled even when spray coverage is suboptimal.

Herbicides such as saflufenacil are also absorbed by the roots. Once absorbed by the roots, saflufenacil is predominantly translocated in the xylem, with some movement in the phloem. Saflufenacil appears to have a higher level of translocation than most other Group G herbicides.

2G.4 Symptoms

Symptoms are rapid leaf bleaching, desiccation and browning (necrosis), which is often localised around the site of droplet contact if spray coverage is suboptimal.

Sublethal rates of acifluorfen may cause a bronzing effect on young leaves.

Droplet spray drift leads to flecking or bleached spots on the leaves.

Symptoms of soil-absorbed herbicide show as rapid chlorosis of newly emerged cotyledons and first leaves followed by rapid necrosis.

VIDEO

Ohio State University Weed Science time lapse of Group G (Group 14 WSSA) herbicide fomesafen sprayed on giant ragweed

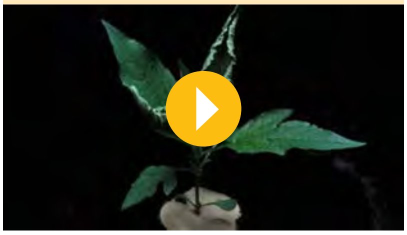

Photo 2: *Flecking or bleached spots due to Affinity (carfentrazone) on wheat.*

Photo: Rural Directions

Photo 3: *Necrosis of navy bean leaves due to Blazer (acifluorfen).*

Photo: DPI&F

Photo 4: *Carfentrazone (Affininty) bleaching affects to a ryegrass leaf.*

Photo: Chris Preston

Photo 5: *Salflufenacil (Sharpen) affecting sunflowers.*

Photo: Chris Preston

2G.4.1 Timeframe for symptoms and plant death

Rate of development of symptoms and subsequent damage and death depend on the plant species, herbicide dose, age and size of plant, and rate of plant growth.

Symptoms can be observed within a few hours of post-emergence application. Plant death occurs from as early as two–four days after treatment.

2G.5 Crop selectivity

Rapid metabolism of the herbicide plays a major role in tolerance; susceptible species cannot metabolise these herbicides. In the case of post-emergent herbicides such as carfentrazone, the herbicide is rapidly metabolised by wheat, maize, soybeans and potatoes.

Butafenacil and oxyfluorfen are non-selective because they are very slowly metabolised by the plant, or not metabolised.

Crop selectivity is also controlled by lower levels of translocation in tolerant species, such as in the roots of maize plants. See Table 2 for details of uses of Group G herbicides.

Table 2: *Differences in efficacy between Group G chemical classes.*

Group G class	Herbicide	Crops	Weeds
Diphenyl ethers	Acifluorfen	Adzuki beans, mungbeans, peanuts, soybeans, green beans, seed crops of siratro and stylo	Post-emergent control of a range of broadleaf weeds up to eight true leaves; some grasses pre-emergence at high application rate
	Oxyfluorfen	Brassicas (broccoli, cabbages, cauliflower), coffee, tree plantations, fruit orchards, nut trees, olive trees, *Duboisia* (corkwood tree), grapevines, pyrethrum, fallow, tobacco	Annual grasses and broadleaf weeds Spike for knockdown herbicides up to 4-leaf weeds At high application rates acts as a residual herbicide
N-phenylphthalimides	Flumioxazin	Prior to sowing barley, chickpeas, faba beans, field peas, lentils, lupins, maize, mungbeans, oats, sorghum, soybeans, sunflowers and wheat; cotton, sugarcane	Rapid knockdown of a range of grass and broadleaf weeds as a knockdown spike
Oxadiazoles	Oxadiargyl	Currently not registered in Australia	Pre- and early post-emergent control of grasses and broadleaf weeds
	Oxadiazon	Woody ornamental shrubs and trees in nurseries and turf	Pre-emergent control of a wide range of annual grasses and broadleaf weeds
Phenylpyrazole	Pyraflufen-ethyl	Pre-sowing knockdown when premixed with glyphosate Post-emergent control in wheat, barley, triticale, oats and clover pastures	Spike added to glyphosate to speed brown-out of grasses and broadleaf weeds and to improve control of marshmallow and wild radish
Pyrimidindiones	Butafenacil	Premix with glyphosate or triasulfuron: with glyphosate prior to sowing cereals, to commence a fallow; with triasulfuron in wheat	Control in a range of annual grasses and broadleaf weeds
	Saflufenacil	Annual crops and forestry plantations, fallows, established citrus, pome and almond orchards; around commercial, industrial, and agricultural buildings and yards; on established lucerne crops, and harvest-aid application in pulse crops	A range of broadleaf weeds including volunteer cotton, small-flowered mallow and fleabane, and grass weeds Also used as a tank-mix spike for knockdown herbicides
Triazolinones:	Carfentrazone	Winter cereals and pyrethrum	Post-emergent broadleaf control Spike with pre-sowing knockdown herbicide
		Water bodies	Aquatic weeds

Often these herbicides are tank-mixed with a knockdown herbicide for pre-emergent control, or carfentrazone and pyraflufen-ethyl are mixed with a phenoxy (Group I) herbicide for post-emergent control of broadleaf weeds in cereal crops.

MORE INFORMATION

See the comprehensive GRDC Spray Application GrowNote for more information.
https://grdc.com.au/Resources/GrowNotes-technical/Spray-Application-Manual

2G.6 Effect of environmental conditions on activity

Various environmental characteristics of Group G herbicides are presented in Table 3.

2G.6.1 Light

Sunlight is essential for these herbicides to work effectively because they affect the plant's photosynthetic system when applied post-emergence.

2G.6.2 Temperature

As temperature increases, the rate of uptake of herbicide increases provided respiration and photosynthesis are not limited by the conditions. However, the total amount of herbicide absorbed does not change.

Warmer temperatures promote plant respiration and photosynthesis, which speeds the action of Group G herbicides.

2G.6.3 Humidity

Low humidity reduces absorption. Relative humidity >65% is recommended for post-emergent applications.

2G.6.4 Soil moisture stress

Reduced photosynthesis and respiration will reduce the efficacy of Group G herbicides.

2G.6.5 Rainfall

Group G herbicides are rapidly absorbed by foliage and strongly absorbed by soil colloids and organic matter.

Saflufenacil has a one-hour rain-fast period. The post-emergent herbicides acifluorfen, carfentrazone and pyraflufen-ethyl have a six-hour rain-fast period.

Table 3: *Environmental characteristics of Group G herbicides.*

Group G class	Active ingredient	Example trade name	Water solubility (mg/L)	Log K_{ow}	Soil persistence (half-life @ 20°C) (days)	Soil mobility (K_{oc}/K_{foc})	Drift potential (Henry's Law constant, 25°C)
Diphenyl ethers	Acifluorfen	Blazer®	250,000	1.18	54	113, moderate	Non-volatile
	Oxyfluorfen	Goal®	0.12	4.86	73	7566, non-mobile	Volatile
N-phenylphthalimides	Flumioxazin	Valor®	0.79	2.55	18	889, moderate	Moderate
Oxadiazoles	Oxadiargyl	No products registered	0.37	3.95	19	1915, moderate	Moderate
	Oxadiazon	Ronstar®	0.57	5.33	165	3200, moderate	Moderate
Phenylpyrazole	Pyraflufen	Ecopar®	1	4.87	7	1480, moderate	Moderate
Pyrimidindiones	Butafenacil	One constituent of Logran® B-Power®	10	3.2	1	365, moderate	Non-volatile
	Saflufenacil	Sharpen®	2100	2.6	20	9–55, mobile	Non-volatile
Triazolinones	Carfentrazone-ethyl	Affinity® Force	29	3.7	0.5	886, slight	Non-volatile

Log K_{ow}, ratio of herbicide that is soluble in octanol (organic solvent) v. water; it is a good indicator of the lipophilic or hydrophilic nature of a herbicide; the larger the log K_{ow} value the more lipophilic the herbicide; herbicides with values between –1 and 1 should move in the phloem following foliar application. K_{oc}/K_{foc}: >1000, binds strongly to soil; <500, moves in water. Solubility will vary with temperature and to a lesser degree pH.

Source: Pesticides Properties Database, http://sitem.herts.ac.uk/aeru/ppdb/en/index.htm

2G.7 Spray application

Group G herbicides have limited translocation because of their rapid action; therefore, post-emergent spray coverage must be 15% as measured on water-sensitive paper.

Saflufenacil plus glyphosate and post-emergent herbicides mixed with a phenoxy (Group I) herbicide must be applied as a coarse spray quality or larger. This requires an application volume of 50–80 litres per hectare (depending on label) to obtain the level of coverage needed.

Older herbicides such as acifluorfen recommend an application volume of 100–300 litres per hectare.

MORE INFORMATION

See the comprehensive GRDC Spray Application GrowNote for more information.
https://grdc.com.au/Resources/GrowNotes-technical/Spray-Application-Manual

See the GRDC Adjuvants Booklet
https://grdc.com.au/resources-and-publications/all-publications/publications/2015/04/adjuvants-booklet

2G.7.1 Adjuvants

The use of adjuvants with in-crop post-emergent Group G herbicides is not recommended, or there is a warning of increased crop damage. On the other hand, use of an adjuvant with knockdown herbicides is often recommended.

Read the label for specific recommendations.

2G.7.2 Water quality

Water quality is generally not an issue with Group G herbicides; however, water quality must be taken into account when tank-mixed with another product, which might be affected.

2G.8 Further reading

Caseley JC (1987) Effects of weather on herbicide activity. In 'Eighth Australian Weeds Conference'. pp. 386–394.

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Herbicide Group H modes of action

The Group H Mode of Action (MoA) herbicides block carotene synthesis by inhibiting the enzyme 4-hydroxyphenyl-pyruvate dioxygenase (HPPD). Symptoms include the bleaching of new growth.

Group H herbicides are also classified as Group 27 by the global Herbicide Resistance Action Committee (HRAC) and Group F2 by the Weed Science Society of America (WSSA) (http://hrac.tsstaging.com/tools/classification-lookup).

There are three chemical classes within the Group H MoA as shown in Table 1. These classes are different types of chemicals; however, they affect the same biochemical pathways in the plant. The triketone herbicide mesotrione is currently not registered for use in Australia.

Table 1: *Herbicides included in Group H.*

Chemical class	Active ingredient	Product examples
Isoxazoles	Isoxaflutole	Balance®
Pyrazoles	Benzofenap	Taipan®
	Pyrasulfotole	Precept®, Velocity®
Triketone	Bicyclopyrone	Talinor™
	Mesotrione (not registered in Australia)	Callisto®, Tenacity®

Precept® and Velocity® contain more than one active constituent.

Source: http://www.croplife.org.au/resistance-strategy/herbicide-mode-of-action-groups/

Isoxaflutole was first commercialised in 1998 and is used in fallow, chickpeas and sugarcane for the pre-emergent control of a range of annual grasses and broadleaf weeds. Benzofenap was first registered in Japan in 1981 and is now used in flooded rice in Australia. Pyrasulfotole was commercialised in Australia in 2009 and is formulated with either MCPA or bromoxynil to control a range of post-emergent broadleaf weeds in winter cereals.

Mesotrione is a mimic of the natural herbicide leptospermone, which is secreted by the crimson bottlebrush (*Callistemon citrinus*) and some other members of the myrtle family. It was commercialised in the northern hemisphere in 2001.

Bicyclopyrone was registered in 2015 and released in Australia in 2017 in a pre-mix with bromoxynil (Group C).

2H.1 Mode of action and biochemical pathways

Group H herbicides block the production of carotenoids by inhibiting the enzyme HPPD. This enzyme is essential for the production of plastoquinone, which is also a co-factor in the biosynthesis of carotene (Figure 1).

Carotenoids play an important part in photosynthesis by capturing light energy and transferring it to the chlorophyll. Carotenoids also play three protective major roles in the photosynthetic apparatus. The first role is to quench triplet chlorophyll molecules back to the ground state. The second is to quench singlet oxygen molecules back to the normal and non-destructive triplet state. The third is to moderate the photosystem reaction centres in bright light. If triplet chlorophyll is not moderated, it will produce reactive oxygen, which destroys the photosynthetic apparatus within the thylakoid membrane. Destruction of chlorophyll leads to bleaching of the plant tissue.

Plants treated with Group H herbicides have lower levels of carotenoids, allowing the oxygen radicals to remove hydrogen from membrane fatty acids, producing a lipid radical. These lipid radicals interact with molecular oxygen to form peroxidised and other lipid radicals. This creates a chain reaction of lipid peroxidisation that destroys chlorophyll and membrane lipids. Proteins are also damaged. The destruction of integral membrane components leads to leaky membranes and rapid tissue desiccation.

For a detailed explanation go to: Plant & Soil Sciences eLibrary Lessons: Inhibitors of carotenoid biosynthesis.

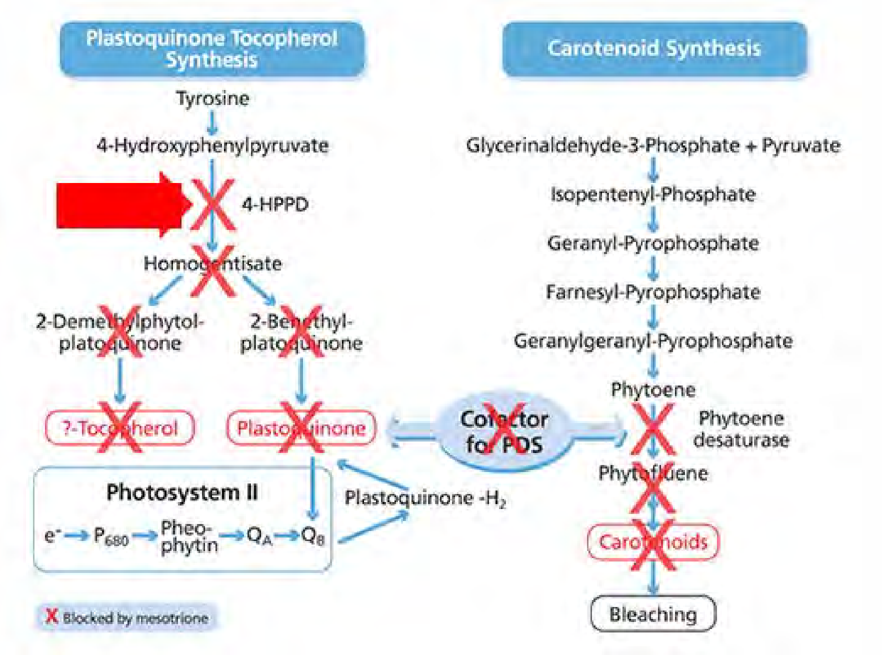

Figure 1: *Biosynthesis pathways affected by Group H herbicides.*

2H.2 Absorption into the plant

Group H herbicides range in water solubility and tend to be lipophilic (Table 2). Isoxaflutole has low water solubility and is lipophilic, whereas its active form diketonitrile (DKN) is water-soluble and highly mobile in the plant. The greater lipophilicity of isoxaflutole gives greater uptake by seed, shoot and root tissues. DKN is formed rapidly in plants following uptake by the roots and shoots. Isoxaflutole also undergoes conversion to DKN in the soil.

Benzofenap is absorbed by roots and meristems of small plants.

Pyrasulfotole and bicyclopyrone are highly water-soluble. Once inside the plant, however, they are not well translocated within the phloem.

Table 2: *Environmental characteristics of Group H herbicides.*

Group H class	Active ingredient	Example trade name	Water solubility (mg/L)	Log K_{ow}	Soil persistence (half-life @ 20°C) (days)	Soil mobility (K_{oc}/K_{foc})	Volatility (Henry's Law constant, 25°C)
Isoxazoles	Isoxaflutole	Balance®	6.2	2.34	0.5–3	145, low	Non-volatile
	DKN	(active molecule)	326	0.4	20–30	Moderate	Non-volatile
Pyrazoles	Benzofenap	Taipan®	0.13	4.69	38	Immobile	Moderate
	Pyrasulfotole	Velocity®*	69,100	–1.36	55	368, moderate	
Triketone	Bicyclopyrone	No products registered	119,000	?	213	Highly mobile	Non-volatile
	Mesotrione	Callisto® (no products registered in Australia)	1500	0.11	5	122, moderate	Non-volatile

Diketonitrile (DKN) is the active form of isoxaflutole. Log K_{ow}, ratio of herbicide that is soluble in octanol (organic solvent) v. water; it is a good indicator of the lipophilic or hydrophilic nature of a herbicide; the larger the log K_{ow} value the more lipophilic the herbicide; herbicides with values between –1 and 1 should move in the phloem following foliar application. K_{oc}/K_{foc}, >1000, binds strongly to soil; <500, moves in water.

Source: Pesticides Properties Database, http://sitem.herts.ac.uk/aeru/ppdb/en/index.htm

2H.3 Translocation within the plant

There is limited translocation from the leaves to other parts of the plant. Root uptake and translocation is via the xylem.

Without conversion to DKN, isoxaflutole would not be translocated within the plant. Translocation of benzofenap, pyrasulfotole and bicyclopyrone within the plant is limited.

2H.4 Symptoms

Symptoms on larger plants begin with bleaching of the new growth. This bleaching and yellowing spreads through the plant, leading to necrosis (browning).

With soil-applied herbicide, susceptible weeds germinate and emerge but show immediate chlorosis followed by irregular patches of white and/or mauve–pink discoloration. The chlorosis spreads with the aerial growth and the plants become necrotic and die.

VIDEO

Ohio State University Weed Science time lapse of effect of mesotrione on waterhemp.

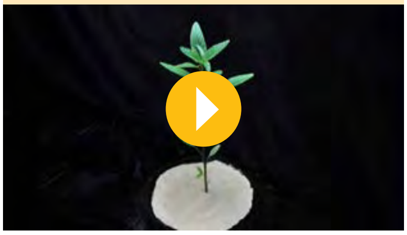

Photo 1: *Balance (Isoxaflutole) in faba beans causing yellowing and necrosis.*

Photo: Andrew Storrie, Agronomo

Photo 2: *Balance (isoxaflutole) damage to chickpeas causing necrosis.*

Photo: Kevin Moore NSW DPI

2H.4.1 Timeframe for symptoms and plant death

Rate of symptom development and subsequent damage and death depend on the plant species, herbicide dose, age and size of plant, and rate of plant growth. Death occurs from as early as two weeks to four to six weeks after treatment.

2H.5 Crop selectivity

Selectivity appears to be a function of speed of degradation in susceptible compared with tolerant species, as well as differences between varieties within a species, as well as separation of crop plants from treated soil (Table 3).

In both plants and soil, the DKN is converted to the herbicidally inactive benzoic acid. This degradation is more rapid in maize than in susceptible weed species, and this contributes to the mechanism of selectivity, together with the greater sowing depth of the crop.

Photo 3: *Photo showing the difference between chickpea varieties to tolerance to Balance (isoxaflutole) herbicide.*

Photo: Kevin Moore, NSW DPI

Planting depth has been shown to influence the level of crop damage and is influenced by soil pH, clay content, organic matter, and time and intensity of rain after application.

Pyrasulfotole and bicyclopyrone have a safener added to the mix to speed degradation within crop plants.

Maize plants can rapidly metabolise bicyclopyrone into inactive compounds, and this contributes to the herbicide's selectivity in killing weeds.

Table 3: *Differences in efficacy between Group H chemical classes.*

Group H class	Herbicide example	Crops	Weeds
Isoxazoles	Isoxaflutole	Sugarcane, chickpeas, fallow	All pre-emergent applications in Australia, except for sugarcane Fleabane (*Conyza bonariensis*), sowthistle (*Sonchus oleraceus*), feathertop Rhodes grass (*Chloris virgata*), cape weed, *Crassula* spp., Indian hedge, mustard, medic, prickly lettuce, turnip weed and wild radish; suppression of *Echinochloa* spp., deadnettle, slender celery
Pyrazoles	Benzofenap	Rice	Arrowhead, *Alisma* spp., starfruit, water plantain; suppression of *Cyperus difformis*
	Pyrasulfotole	Wheat, barley, cereal rye and triticale; oats (Precept®)	Post-emergent control of broadleaf weeds
Triketone	Bicyclopyrone	Talinor™, registered in Wheat and Barley	Post-emergent control of broadleaf weeds
	Mesotrione	Not registered in Australia	Pre-emergent control of annual grasses and broadleaf weeds

Pyrasulfotole and bicyclopyrone can be formulated with either a Group C or Group I herbicide, or both, to broaden the weed-control spectrum in grass crops.

MORE INFORMATION

See the comprehensive GRDC Spray Application GrowNote for more information.
https://grdc.com.au/Resources/GrowNotes-technical/Spray-Application-Manual

2H.6 Effect of environmental conditions on activity

Because Group H herbicides are poorly translocated, they act as contact herbicides when applied following weed emergence. Absorption of these herbicides via the roots is important for effective control; therefore, available soil moisture is a critical factor in determining the efficacy of these herbicides.

2H.6.1 Light

Light intensity will influence the speed of development of the symptoms.

Pyrasulfotole is recommended to be applied at least one hour before sunset, particularly if followed by low night temperatures.

Isoxaflutole is stable on the soil surface and not subject to photodegradation.

2H.6.2 Temperature

As temperature increases, the rate of photosynthesis increases, which speeds the production of radicals within the photosynthetic system. Frosts and cold stress will reduce the effectiveness of these herbicides and can lead to increased crop damage.

2H.6.3 Humidity

Plants growing in conditions of higher humidity have less epidermal wax on the leaf surface than plants growing in low humidity. These conditions will increase the amount of foliar-applied herbicide entering the plant.

2H.6.4 Soil moisture stress

Moisture-stressed plants have thicker cuticles, which will slow the absorption of foliar-applied Group H herbicides. Addition of certain adjuvants can assist herbicide absorption into the plant.

Adequate moisture is required at the surface soil to enable root absorption of isoxaflutole, its active form DKN, and pyrasulfotole. Drying of the surface soil will reduce the level of weed control when using these herbicides.

Isoxaflutole requires moisture at the soil surface, where it can be taken up by surface-germinating weed seeds to be converted to the more soluble DKN.

Benzofenap is applied to flooded rice bays, so the herbicide diffuses from the water into the weeds.

2H.6.5 Rainfall

The rain-fast period for foliar application of pyrasulfotole is two hours, suggesting rapid binding to cuticular waxes.

Rain is required to incorporate isoxaflutole into the surface soil.

Significant rain following application of bicyclopyrone application can lead to its movement down the profile into the root-zone.

MORE INFORMATION

See the comprehensive GRDC Spray Application GrowNote for more information.
https://grdc.com.au/Resources/GrowNotes-technical/Spray-Application-Manual

See the GRDC Adjuvants Booklet
https://grdc.com.au/resources-and-publications/all-publications/publications/2015/04/adjuvants-booklet

2H.7 Spray application

Pyrasulfotole requires very good coverage because this herbicide is effectively a contact herbicide with little downward translocation. Labels recommend applying 50–150 litres per hectare for optimum coverage with medium quality.

Target coverage should be 10–15% as measured with water-sensitive paper.

Soil-applied herbicides need even coverage; however, they can be applied in a coarse to extremely coarse spray quality. If tank-mixed with a knockdown herbicide, they should be applied in the relevant spray quality for that knockdown herbicide.

2H.7.1 Adjuvants

Addition of adjuvants to isoxaflutole and benzofenap is not required because of their use pattern in Australia. Research in North America has shown improved post-emergent weed control when isoxaflutole is applied with a methylated seed oil adjuvant; however, this can increase crop phytotoxicity.

Pyrasulfotole requires crop oil adjuvant except when mixed with the grass herbicide Wildcat®, when a non-ionic surfactant is recommended.

2H.7.2 Water quality

Water quality has little effect on Group H herbicides, provided it is within reasonable quality parameters.

2H.8 Further reading

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Herbicide Group I modes of action

The Group I Mode of Action (MoA) herbicides are synthetic plant hormones or auxins primarily targeting broadleaf (dicot) weeds, but some monocots as well.

They are also classified as Group O by the global Herbicide Resistance Action Committee (HRAC) and Group 4 by the Weed Science Society of America (WSSA) (http://hrac.tsstaging.com/tools/classification-lookup).

There are five chemical classes within the Group I MoA as shown in Table 1. These classes are different types of chemicals; however, they affect the same biochemical pathways in the plant.

Table 1: *Herbicides included in Group I.*

Chemical class	Active ingredient	Product examples
Arylpicolinates	Halauxifen	Paradigm™ (PM)
Benzoic acids	Dicamba	Broadside® (PM), Kamba® M (PM)
Phenoxycarboxylic acids (phenoxys)	2,4-D	Amicide®, Estercide®
	2,4-DB	Trifolamine®
	Dichlorprop	Lantana 600
	MCPA	MCPA, Agtryne® MA (PM), Buctril® MA (PM)
	MCPB	Nufarm MCPB-400
	Mecoprop	Methar Tri-Kombi® (PM)
Pyridine carboxylic acids (pyridines)	Aminopyralid	FallowBoss™ Tordon™ (PM), ForageMax™ (PM), Grazon™ Extra (PM), Hotshot™ (PM), Vigilant™ II (PM)
	Clopyralid	Lontrel™, Spearhead® (PM)
	Fluroxypyr	Starane®, Hotshot™ (PM)
	Picloram	Tordon™ 75-D (PM), FallowBoss™ Tordon™ (PM), Grazon™ Extra (PM)
	Triclopyr	Garlon™
Quinoline carboxylic acids	Quinclorac	Drive®

PM, Product contains more than one active constituent.

Source: http://www.croplife.org.au/resistance-strategy/herbicide-mode-of-action-groups/

The Group I herbicide 2,4-D was commercially released after World War II and was the first of the 'new' synthetic herbicides that have been the basis of weed-control practices for the last 70 years.

Global use of Group I herbicides is an estimated 200 million hectares annually. They are used as post-emergent herbicides in a wide range of crops, as well as for fallow and non-agricultural weed control. Some have soil residual properties.

21.1 Mode of action and biochemical pathways

Group I herbicides are synthetic plant hormones (auxins) and mimic the key plant hormone indole-3-acetic acid (IAA). These herbicides are less prone to degradation or inactivation than the natural hormone and cause increased activity of the auxin-responsive genes, particularly those producing abscisic acid and ethylene. This leads to unregulated plant cell growth then to distortion of growing parts, growth inhibition, senescence and tissue decay in sensitive broadleaf plants (dicots) and a small range of monocots (grass-like plants) such as sedges.

The production of high levels of ethylene and the reduction in photosynthesis resulting from stomatal closure by abscisic acid leads to the formation of high levels of reactive oxygen molecules, which in turn cause tissue deformation and twisting (epinasty).

Photo 1: *Twisting (epinasty) from Group I drift in peanuts.*

Photo: DPI&F

One chemical class—the quinoline carboxylic acids—also has activity on some grasses as well as broadleaf weeds. In sensitive grasses, there is a rapid increase in ethylene, carbon dioxide and nitrates plus an accumulation of cyanide in the plant tissues.

For a detailed explanation, go to Plant & Soil Science eLibrary: Auxin and auxinic herbicide mechanism(s) of action.

2I.2 Absorption into the plant

Most Group I herbicides such as 2,4-D are formulated as 'pro-herbicides' to enable better absorption by the plant because the active acid forms have low solubility in water. Therefore, they are formulated either as a salt (sodium, potassium, amine or choline) or as an ester to improve movement into the plant. Quinclorac is the exception and is formulated as an acid.

The different formulations are converted to the active acid form once inside the plant.

Group I herbicides can be absorbed through leaves, stems and shoots as well as roots.

Salt formulations are water-soluble (Table 2), meaning that they move through the cuticle and epidermis via the 'aqueous route', which is like the holes in a sponge. This route into the leaf tends to be relatively slow. For salt (polar) formulations to enter the leaf, they must remain dissolved in the water droplet. When the water has evaporated from the droplet, a crystalline deposit remains and movement into the leaf stops until it can be re-wet by high humidity, dew or light rain.

Ester formulations, which are lipophilic (fat loving), rapidly absorb into the cuticular waxes on the leaf surface and move to the leaf epidermis via diffusion. Initial absorption is very fast, making ester formulations less affected by water quality and environmental conditions.

Salt formulations of these herbicides are readily absorbed by plant roots.

Photo 2: *Chickpeas affected by 2,4-D soil residues.*

Photo: Kevin Moore, NSW DPI

The herbicide quinclorac is also absorbed from the soil through the coleoptiles of emerging grasses.

Table 2: *Environmental characteristics of Group I herbicides.*

Group I class	Active ingredient	Example trade name	Water solubility (mg/L)	Log K_{ow}	Soil persistence (half-life @ 20°C) (days)	Soil mobility (K_{oc}/K_{foc})	Drift potential (Henry's Law constant, 25°C)
Arylpicolinates	halauxifen methyl	Arylex®	1.83	3.76	1.3 (1 – 2)	995 (190 – 1812)	1.5×10^{-5}
Benzoic acids	Dicamba (DMA)	One constituent of Broadside®	250,000, high	0.29	4 (3–5)	12.4, very mobile	Non-volatile
Phenoxys	2,4-D	Amicide®	24,300, high	2.81	29 (22–38)	0.7, very mobile	Non-volatile
	2,4-DB	Trifolamine®	4,385, high	1.22	16 (7–24)	500, moderate	Non-volatile
	MCPA	MCPA	29,390, high	–0.81	25 (7–41)	110, mobile	Non-volatile
Pyridines	Aminopyralid	Hotshot™	2480, high	–2.87	21 (8–35)	8.3, very mobile	Non-volatile
	Clopyralid	Lontrel™	143,000, high	–2.63	11 (2–24)	5, very mobile	Non-volatile
	Fluroxypyr	Starane®	65,000, high	–1.5	51 (34–68)	68, mobile	Non-volatile
	Triclopyr	Garlon™	1,000,000, high	4.62	30 (7–54)	27, mobile	Non-volatile
	Picloram	Tordon™	560	1.4	36 (20–49)	13, very mobile	Non-volatile
Quinolones	Quinclorac	Drive®	0.065, low	0.07		50, mobile	Non-volatile

Log K_{ow}, ratio of herbicide that is soluble in octanol (organic solvent) v. water; it is a good indicator of the lipophilic or hydrophilic nature of a herbicide; the larger the log K_{ow} value the more lipophilic the herbicide; herbicides with values between –1 and 1 should move in the phloem following foliar application. K_{oc}/K_{foc}: >1000, binds strongly to soil; <500, moves in water. Different formulations of each herbicide, such as the acid, salt and ester forms, will have different chemical and therefore environmental, compatibility and behavioural characteristics. Solubility will vary with temperature and to a lesser degree pH.

Source: Pesticides Properties Database - http://sitem.herts.ac.uk/aeru/ppdb/en/index.htm and Dow AgroSciences Australia Ltd

21.3 Vapour drift risk

Vapour drift risk is affected by a complex series of interactions including:

- molecular weight of herbicide
- herbicide formulation: acid < sodium salt < amine salt < ester
- amount of herbicide applied per hectare and total area treated
- tank mix partners such as ammonium sulfate
- meteorological conditions: air and soil temperature, humidity, wetting–drying of plants and soil, temperature inversions trapping herbicide vapour
- characteristics of surfaces where droplets or deposits land: soil, stubble, plant leaves (varies with species)
- size of droplets or deposits
- sensitivity of neighbouring crops and vegetation such as cotton, tomatoes, grape vines.

For most situations, vapour drift following herbicide application is a minor risk compared with droplet and particle drift during herbicide application. An analysis of the hazards and risks to neighbouring crops and sensitive areas should be conducted before spraying any herbicides.

21.4 Translocation within the plant

Group I herbicides have great mobility within the plant because they are intermediate in their hydrophilic and hydrophobic properties, allowing them to move through oily cell membranes and watery cytoplasm. This permits them to move both upward to the leaves and growing points and downward toward the roots of the plant.

They move rapidly through the cytoplasm of plant cells (the symplastic system) including the phloem. With root uptake, these herbicides follow the transpiration pathway, primarily within the sap within cell walls and spaces between the cells (the apoplast) (Figure 1). (For definitions of symplastic and apoplastic movement, see Herbicide GrowNotes: Group A)

Rapid absorption and translocation mean that cultivation or crop planting can occur within 24 hours of application with minimal effects on herbicide efficacy.

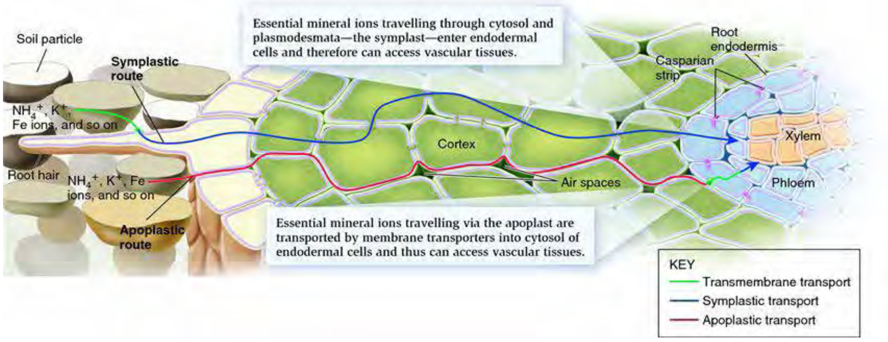


Figure 1: *The path for root uptake.*

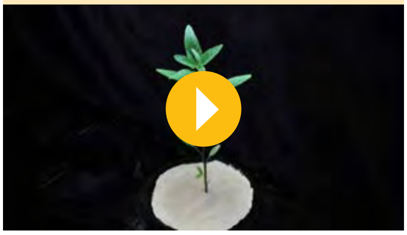
Source: Biologyforums.com

21.5 Cellular absorption: passive diffusion and active absorption

The most common type of cellular absorption is passive, whereby the herbicide moves from an area of higher concentration (symplast) to an area of lower concentration in the cell.

VIDEO

Ohio State University Weed Science: Time lapse of effect of foliar application of 2,4-D on velvetleaf plant.



The herbicide 2,4-D can also be absorbed into plant cells via active absorption, which moves the herbicide molecule across the cell membrane against the concentration gradient. This process increases the concentration of herbicide within the cell and it is facilitated by a protein carrier located in the cell membrane. For a detailed explanation of this process, go to Plant & Soil Science eLibrary: Cellular absorption of herbicides—active absorption.

Once inside the living plant tissue, the herbicides move inside the phloem with sugars and amino acids towards areas of growth and/or storage. These herbicides then accumulate in the growing tips of roots and shoots (meristems) where they interrupt growth.

Group I herbicides are also weak acids. Weak acids are compounds containing a functional group, usually a carboxylic acid. This functional group gains or loses a hydrogen ion depending on the pH of the surrounding solution (for more details, see Herbicide GrowNotes: Group A).

21.6 Symptoms

Symptoms are first exhibited and most severe on the new growth. Symptoms exhibited in dicot species include bending and twisting of young stems and petioles, swelling of stems and nodes, leaf cupping and curling. The area of newly forming leaves is restricted, with them becoming narrow and strap-like.

Growth slows, with growing points yellowing followed by wilting and death. Older growth reddens.

The herbicide quinclorac is also active on several grass species. Symptoms on grasses include cessation of growth with increased yellowing of the youngest leaves followed by wilting and browning of the entire shoot.

Photo 3: *Twisted canola stems from 2,4-D.*

Photo: David Pfeiffer

Photo 4: *The effects of 2,4-D on wheat heads.*

Photo: Tony Cook

Photo 5: *Tordon damage in mungbeans.*

Photo: DPI&F

Photo 6: *Chickpeas with twisting and deformity from phenoxys.*

Photo: Kevin Moore, NSW DPI

Photo 7: *Picloram (Tordon) residues in faba beans.*

Photo: Rohan Brill, NSW DPI

21.6.1 Timeframe for symptoms and plant death

Rate of development of symptoms and subsequent damage and death depend on the plant species, herbicide dose, age and size of plant, and rate of plant growth. Death occurs from as early as two weeks to around four–six weeks post-application:

- Within the first few hours of application is the stimulation phase. Production of ethylene increases, leading to twisting of new growth.
- After 24 hours, root and shoot growth stops and green pigmentation intensifies. Stomata close, leading to a reduction in transpiration and an increase in the concentration of reactive oxygen molecules. New growth becomes severely twisted.
- Chloroplasts within the cells are damaged and plant tissue progressively becomes more yellow. Cell membranes and the plant vascular system break down, leading to wilting and plant death.

21.7 Crop selectivity

Plants that are tolerant of Group I herbicides detoxify them by using P450 enzymes, which replace a chlorine group on the aromatic ring with a hydroxyl group. This then allows joining (conjugation) with glucose or other large molecules. Amino acids can also bind to a side chain of the herbicide molecule. These large molecules have no herbicidal activity and are then further broken down to carbon dioxide and other products.

Some plants that are not affected by Group I herbicides could also have receptor sites that do not allow binding of the herbicide molecule.

Because of differences in efficacy between the chemical classes (Table 3), they are often used as pre-mixes or tank mixes to broaden the number of species controlled. For example, the phenoxy MCPA is often combined with arylpicolinates, benzoic acids and pyridines to broaden the control spectrum.

Table 3: *Differences in efficacy of Group I chemical classes according to plant family.*

Group I class	Dicot families	Non-grass monocots	Grasses
Arylpicolinates	Boraginaceae Fabaceae Fumariaceae Rubiaceae		
Benzoic acids	Amaranthaceae Fabaceae Polygonaceae NOT Brassicaceae		
Phenoxys	Amaranthaceae Asteraceae Boraginaceae Chenopodiaceae Cucurbitaceae Geraniaceae Lamiaceae Polygonaceae Rubiaceae Solanaceae	Crassulaceae (e.g. stonecrop) Cyperaceae (e.g. sedges)	
Pyridines	Asteraceae Fabaceae Malvaceae Rosaceae Solanaceae	Cactaceae Commelinaceae Crassulaceae	

MORE INFORMATION

See the comprehensive GRDC Spray Application GrowNote for more information.
https://grdc.com.au/Resources/GrowNotes-technical/Spray-Application-Manual

Group I class	Dicot families	Non-grass monocots	Grasses
Quinclorac	Convolvulaceae Fabaceae Rubiaceae (e.g. cleavers) NOT Brassicaceae	Cyperaceae (e.g. *C. esculentus*) Commelinaceae (e.g. *Commelina* spp.)	*Brachiaria* spp. *Digitaria* spp. *Echinochloa* spp. *Leptochloa* spp. *Setaria* spp.

21.8 Effect of environmental conditions on activity

Water-soluble (hydrophilic) formulations (i.e. salts) will be more affected by environmental conditions than oil-soluble (lipophilic) formulations such as esters.

Herbicide effectiveness is influenced by the interaction of temperature, humidity and light intensity on the weed species, because this affects transpiration, respiration and leaf surface characteristics.

21.8.1 Light

Conditions of high light intensity can thicken the cuticle of a weed, which will reduce the uptake of water-soluble formulations. Decreasing light intensity, such as occurs in autumn, increases the ratio of shoots to rhizomes in perennial species. This leads to better control through better herbicide interception and more herbicide translocating to the root system. There is also an increase in the amount of assimilates moving into roots and storage organs, which in-turn increases the transport of phloem-mobile herbicides, including those in Group I.

21.8.2 Temperature

As temperature increases, the rate of uptake of herbicide increases provided respiration and photosynthesis are not limited by the conditions. However, the total amount of herbicide absorbed does not change. High temperatures and low available soil moisture reduce herbicide translocation through the shutdown of transpiration.

Optimum temperatures for photosynthesis and respiration are determined by whether the plants use C3 or C4 photosynthesis. C3 plants grow best at temperatures <30°C, whereas C4 plants can actively grow at temperatures up to 35°C and at higher light intensities.

Frost can shut down plant growth for several days and will reduce the translocation of Group I herbicides. Frost following the application of dicamba on oats causes the crop to lay flat on the ground. The crop usually recovers from this condition.

Higher temperatures also increase the likelihood of vapour movement from treated areas. In the USA, herbicide companies have been looking at larger, stable molecules to reduce the potential of vapour drift and have released formulations of dicamba as diglycolamine and BAPMA (N,N-bis(aminopropyl)methylamine) salts and a choline formulation of 2,4-D.

21.8.3 Humidity

Plants growing in conditions of higher humidity have less epidermal wax on the leaf surface than plants growing in low humidity. High humidity hydrates the cuticle, allowing for a continuous aqueous path to the epidermis for salt and amine formulations.

21.8.4 Soil moisture stress

Stressed plants have thicker cuticles, which will absorb and hold more ester formulation herbicide, whereas amine and salt formulations will be prevented from penetrating a thick, dehydrated cuticle. Addition of certain adjuvants can assist herbicide absorption into the plant; however, if it is not actively growing, translocation and efficacy will be limited.

2I.8.5 Rainfall

Both 2,4-D amine salt and ester formulation labels state a six-hour rain-fast period, dicamba sodium salt and dimethylamine salt labels suggest four hours, halauxifen methyl ester three hours, and fluroxypyr methylheptyl ester one hour. As previously noted, esters are rapidly absorbed into the waxy cuticle; however, the amount of cuticle will vary with weed species and growing conditions.

MORE INFORMATION

See the comprehensive GRDC Spray Application GrowNote for more information.
https://grdc.com.au/Resources/GrowNotes-technical/Spray-Application-Manual

See the GRDC Adjuvants Booklet
https://grdc.com.au/resources-and-publications/all-publications/publications/2015/04/adjuvants-booklet

2I.9 Spray application

Group I herbicides are well translocated through the plant. However, all phenoxy herbicides MUST be applied as a coarse or larger quality to minimise the proportion of driftable (fine) droplets produced. For example, any mix that contains MCPA MUST be applied as a minimum coarse spray quality.

Pyridines are recommended to be applied as a medium to coarse droplet in most instances.

Although some labels of non-phenoxy classes such as dicamba and fluroxypyr do not recommend a spray quality, updated online information usually suggests coarse spray quality.

Application volumes can range from 50 to 250 litres per hectare for ground application, and all labels suggest a minimum of 50 litres per hectare.

Target coverage should be 6–15% as measured on water-sensitive paper.

2I.9.1 Adjuvants

Addition of adjuvants is rarely recommended with in-crop applications unless the Group I herbicide is being tank-mixed with a Group A herbicide. Adding extra adjuvant increases the chance of crop damage. Most herbicides will have a certain amount of adjuvant pre-mixed in the drum.

In a fallow or non-crop situation, most labels will recommend a non-ionic surfactant or oil, a non-ionic surfactant such as BS1000™ or a petroleum spray oil + emulsifier blend such as Uptake™. It is recommended that products containing halauxifen also be applied with either a non-ionic surfactant or a petroleum spray oil.

Read the label for recommended use of adjuvants.

The use of dicamba over the top of glyphosate + dicamba-resistant soybeans in the USA has shown that the volatility of dicamba increases significantly if ammonium sulfate is present in the tank mix.

2I.9.2 Water quality

Temperature

Recent research in the USA with a glyphosate + dicamba mix has shown that the control of certain species can be influenced by spray solution temperature. Warmer water (31°C compared with 5°C) gave 26% better control of pitted morning glory (*Ipomoea lacunosa*) and 14% better control of giant ragweed (*Ambrosia trifida*), but had no effect on control of flaxleaf fleabane (*Conyza bonariensis*) or Palmer amaranth (*Amaranthus palmeri*). Increasing the herbicide application rate reduced the temperature effect dramatically.

Low spray mix temperatures can greatly affect tank mixing. This will also depend on water quality, what products are being mixed and the quality of the products used.

pH

The effect of the pH of a spray solution is one of the most widely misunderstood concepts in spray application. The pH will have little effect on efficacy, although Group I herbicides are weak acids and perform slightly better (<5%) in a slightly acid solution. The addition of weak acid herbicides to a tank mix lowers the pH of the solution.

A decrease in the pH of a spray solution by using an unbuffered product such as citric acid can lead to chemicals coming out of suspension and gelling of the spray solution.

Hardness

Water hardness can significantly reduce the efficacy of amine, potassium and sodium salt formulations through the binding of larger cations of calcium and magnesium to the herbicide molecule, making them less soluble.

Research in the USA has shown that the effects of hard water on 2,4-D amine and dicamba are species-dependent, although dicamba was less affected than 2,4-D. Adding ammonium sulfate to the tank prior to 2,4-D improved control of fat hen (*Chenopodium album*), flaxleaf fleabane and redroot amaranth (*Amaranthus retroflexus*). Adding ammonium sulfate before dicamba improved control of fat hen and amaranth, but not fleabane.

Turbidity

Group I herbicides are generally not affected by the presence of clay and particulate matter in the spray solution; however, water of this quality should be treated to reduce blocking of filters and nozzles.

21.10 Further reading

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Herbicide Group J modes of action

The Group J Mode of Action (MoA) herbicides inhibit the synthesis of very-long-chain fatty acid lipids by a different mechanism from Group A herbicides. These fatty acids are necessary for the production of cuticular waxes, especially in the seedling stages of plants, and they affect cell elongation.

Group J is also classified as Group N by the global Herbicide Resistance Action Committee (HRAC) and Group 8 by the Weed Science Society of America (WSSA), although the WSSA rank the chlorocarbonic acids as a Group 26 (http://hrac.tsstaging.com/tools/classification-lookup).

Several of these herbicides were introduced to agriculture in the late 1950s. Many of these herbicides have been removed from use within the European Union because of environmental concerns, such as movement into the ground water, and some (e.g. bensulide) are Schedule 6 poisons.

There are four chemical classes within the Group J MoA as shown in Table 1. These classes are different types of chemicals; however, they affect the same biochemical pathways in the plant.

Table 1: *Herbicides included in Group J.*

Chemical class	Active ingredient	Product examples
Benzofurans	Ethofumesate	Tramat®
Chlorocarbonic acids	2,2-DPA	DalaPon
	Flupropanate	Tussock®
Phosphorodithioates	Bensulide	Exporsan®
Thiocarbamates	EPTC	Eptam®
	Molinate	Ordram®
	Pebulate	Tillam®
	Prosulfocarb	Boxer Gold®
	Thiobencarb	Saturn®
	Triallate	Avadex®, Jetti Duo
	Vernolate	No registered products

Boxer Gold® and Jetti Duo contain more than one active constituent.

Source: http://www.croplife.org.au/resistance-strategy/herbicide-mode-of-action-groups/

The thiocarbamates and 2,2-DPA are the only Group J herbicides used in Australian broadacre agriculture.

Thiocarbamates are soil-applied herbicides used for pre-emergence control of annual grasses, sedges and annual broadleaf weeds (varies with herbicide). Usually, they are incorporated mechanically or with irrigation immediately after application to avoid vapour losses. Ethofumesate is used for pre- and post-emergent selective weed control in beet crops, oilseed poppies, onions and established turf. 2,2-DPA and flupropanate are used as post-emergent herbicides largely for the control of annual and perennial grasses and a range of other species. Flupropanate also has soil residual control of seedling grasses. These two herbicides were reintroduced into use with the spread of the difficult-to-control perennial grass weeds *Sporobolus* and *Nassella* spp.

In Australia, bensulide is used as a pre-emergent herbicide to control winter grass in established turf.

2J.1 Mode of action and biochemical pathways

Group J herbicides block several plant biochemical pathways including biosynthesis of fatty acids, proteins, isoprenoids and flavonoids, as well as inhibiting gibberellin synthesis. Photosynthesis may also be inhibited.

Thiocarbamates block an enzyme in fatty acid biosynthesis, stopping the formation of waxes and suberin, which are important in the formation of the waxy layer on the outside of seedlings and plants as well as in cell elongation.

For detailed explanation, go to Plant & Soil Sciences eLibrary: Inhibitors of fatty acid synthesis and elongation.

2J.2 Absorption into the plant

Group J herbicides are rapidly absorbed by roots and slowly translocated to shoots via the xylem.

Soil-applied herbicide is absorbed by the shoots of emerging seedlings, with some uptake via the roots, depending on the herbicide.

Thiocarbamates enter grass-weed seedlings through the coleoptile and the coleoptile node as it pushes through the treated layer of soil. Triallate can be absorbed by seedlings as a vapour at relatively low soil-moisture contents.

EPTC is absorbed through the hypocotyl hook of broadleaf seedlings. Prosulfocarb is absorbed through the leaves and the roots of seedlings.

2J.3 Translocation within the plant

Group J herbicides are rapidly absorbed by roots and shoots, with either very slow or little translocation from the roots to the shoots.

Translocation of thiocarbamates is limited but primarily occurs in the xylem, the rate being determined by water solubility of the herbicide. For example, EPTC is translocated more readily than triallate.

Both 2,2-DPA and flupropanate are highly water-soluble (Table 2) and will move into the root-zone quickly with rain or irrigation. They are also tightly bound to organic matter.

Table 2: *Environmental characteristics of Group J herbicides.*

Group J class	Active ingredient	Example trade name	Water solubility (mg/L)	Log K_{ow}	Soil persistence (half-life @ 20°C) (days)	Soil mobility (K_{oc}/K_{foc})	Drift potential (Henry's Law constant, 25°C)
Benzofurans	Ethofumesate	Tramat®	50	2.7	38	118, moderate	Non
Chlorocarbonic acids	2,2-DPA sodium	DalaPon	629,000	0.84	30	1, very mobile	Moderate
	Flupropanate sodium	Tussock®	3,900,000	–1.9	365	8.7, very mobile	Non
Phosphorodithioates	Bensulide	Exporsan®	25	4.2	120	3,900, slight	Non
Thiocarbamates	EPTC	Eptam®	370	3.2	18	300, moderate	Non
	Molinate	Ordram®	1,100	2.86	13	190, moderate	Moderate
	Prosulfocarb	Boxer Gold®	13	4.48	10	1693, slight	Non
	Thiobencarb	Saturn®	17	4.23	4	1062, slight	Non
	Triallate	Avadex®	4	4.06	46	3034, slight	Moderate
	Vernolate	No registered products	90	3.84	30	260, moderate	Moderate

Log K_{ow}, ratio of herbicide that is soluble in octanol (organic solvent) v. water; it is a good indicator of the lipophilic or hydrophilic nature of a herbicide; the larger the log K_{ow} value the more lipophilic the herbicide; herbicides with values between –1 and 1 should move in the phloem following foliar application. K_{oc}/K_{foc}: >1000, binds strongly to soil; <500, moves in water.

Source: Pesticides Properties Database, http://sitem.herts.ac.uk/aeru/ppdb/en/index.htm

2J.4 Symptoms

With pre-emergent application, the seedlings usually fail to emerge from the soil. Cell elongation slows quickly. If shoots emerge, they are swollen and bright green. Shoots that emerge from the coleoptile can form a loop because they do not completely emerge.

Thiocarbamates tend to affect shoots more than roots. EPTC also reduces the deposition of cuticular waxes.

Photo 1: *Black oat seedling affected by Avadex (triallate) resulting in a swollen bright green shot.*

Photo: unknown

Photo 2: *Avadex (triallate) damage to a wheat plant showing the looping of the coleoptile.*

Photo: Harm van Rees

2J.4.1 Timeframe for symptoms and plant death

Rate of development of symptoms and subsequent damage and death depend on the plant species, herbicide dose, age and size of plant, and rate of plant growth.

With pre-emergent applications, weed seedlings will rarely emerge and die within two weeks. Depending on the effective dose, seedlings may keep growing and emerge as distorted plants after a couple of weeks.

Post-emergent applications of 2,2-DPA and flupropanate are very slow acting, and symptoms may not show for six weeks to several months for established perennial grasses and sedges.

2J.5 Crop selectivity

Selectivity is obtained with thiocarbamates by herbicide placement, usually in a treated zone above crop seeds with the physical separation of crop seed and seedlings from the herbicide-treated soil. Tolerant plants rapidly metabolise the herbicides, whereas susceptible plants activate the parent compound (some herbicides) so that it becomes herbicidally active (Table 3).

Table 3: *Differences in efficacy between Group J chemical classes.*

Group J class	Herbicide	Crops	Weeds
Benzofurans	Ethofumesate	Beets, onions, oilseed poppies, turf	Pre- and post-emergent control of a range of annual grasses and broadleaf weeds
Chlorocarbonic acids	2,2-DPA	Range of permanent horticulture and non-crop areas; also sugarcane, cotton, potatoes, sunflower, maize, soybeans, tobacco	Non-selective control of annual and perennial grasses, sedges and cumbungi
	Flupropanate	Non-crop areas, pastures, wooded areas	Perennial grasses such as *Sporobolus* spp. and *Nassella* spp.
Phosphorodithioates	Bensulide	Bowling and golf greens	Winter grass (*Poa annua*)
Thiocarbamates	EPTC	Beans, potatoes, maize, sweet corn, dryland safflower, dryland oilseed rape, furrow-sown sunflower, green beans, lucerne, Duboisia, lotus, non-crop areas	Pre-emergent control of a range of grass and broadleaf weeds
	Molinate	Rice	Post-emergent control of annual grasses
	Prosulfocarb	Wheat, barley, chickpeas, Faba beans, lentils, field peas, lupins, potatoes	Annual ryegrass, *Vulpia* spp., *Crassula* spp., suppression of barley grass, and others
	Thiobencarb	Rice (Amaroo variety only, aerial-sown into flooded bay)	Apply to dry soil and flood bays after application: barnyard grass and dirty Dora
	Triallate	Wheat, barley, triticale, canola, chickpeas, faba beans, lupins, field peas, linseed, safflower	Pre-emergent control of a range of annual grass and broadleaf weeds

Triallate is tank-mixed with trifluralin (and is available formulated with trifluralin as Jetti Duo) to broaden the weed-control spectrum. Prosulfocarb is pre-mixed with S-metolachlor (Group K) to broaden the spectrum and give more reliable control; the S-metolachlor is more water-soluble and helps incorporation with rainfall.

2J.6 Effect of environmental conditions on activity

These herbicides are lipophilic (see Table 3) and tend to be bound in soils with higher levels of organic matter.

MORE INFORMATION

See the comprehensive GRDC Spray Application GrowNote for more information.

https://grdc.com.au/Resources/GrowNotes-technical/Spray-Application-Manual

They also tend to have low levels of water solubility, except for 2,2-DPA and flupropanate, so they tend to stay in the surface soil and need to be mechanically incorporated or moved in by irrigation or rainfall. Seedlings that germinate above the herbicide layer with usually continue to grow.

Most Group J herbicides are degraded in the soil by microbes.

2J.6.1 Light

Photodegradation is not a major path of breakdown of these herbicides.

2J.6.2 Temperature

Temperature can affect the volatility of Group J herbicides when they are on the soil surface, particularly triallate.

Warmer soil temperatures promote plant growth, which speeds the action of Group J herbicides.

2J.6.3 Humidity

Humidity has little effect on the action of these herbicides.

2J.6.4 Soil moisture

Owing to the low solubility of these herbicides, adequate soil moisture is essential for absorption by seedlings and plant roots.

Although triallate is activated by low levels of soil moisture, there must be sufficient soil moisture for the weeds to germinate and grow for it to be affective.

MORE INFORMATION

See the comprehensive GRDC Spray Application GrowNote for more information.

https://grdc.com.au/Resources/GrowNotes-technical/Spray-Application-Manual

2J.6.5 Rainfall

Despite triallate and prosulfocarb having lower levels of water solubility, rainfall will assist incorporation.

2J.7 Spray application

Group J herbicides have limited translocation because of their lipophilic characteristics. Triallate and prosulfocarb need to make contact with the soil, so should be applied as a coarse spray quality with an application volume that gives good crop residue penetration; for example, the Avadex® (triallate) label states 40–100 litres per hectare, and Boxer Gold® (prosulfocarb) a minimum of 50 but recommendation of 70 litres per hectare.

Large soil clods reduce the effective coverage of these herbicides and such situations should be avoided.

2J.7.1 Adjuvants

The only truly post-emergent herbicide in this group is 2,2-DPA, and it requires a non-ionic surfactant.

2J.7.2 Water quality

Water quality is generally not an issue with Group J herbicides. However, it must be taken into account when tank-mixing with another product because water quality may affect the tank-mix partner.

2J.8 Further reading

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Herbicide Group K modes of action

The Group K Mode of Action (MoA) herbicides inhibit very-long-chain fatty acid (VLCFA) synthesis within the plastids (double-membrane organelles within cells), although the precise enzymatic steps are not known.

These herbicides are also classified as Group K by the global Herbicide Resistance Action Committee (HRAC) and as Group 15 by the Weed Science Society of America (WSSA) (http://hrac.tsstaging.com/tools/classification-lookup).

Group K herbicides were first commercially released in 1969, with alachlor. Several of these herbicides are now banned in the European Union owing to their potential to contaminate groundwater.

Chloroacetamides are widely used around the world, with metolachlor and S-metolachlor used in maize, sorghum and cotton, as well as nursery and landscape plantings and in turf. In North America, s-metolachlor can be applied through travelling irrigators and in liquid or dry bulk fertiliser.

Pyroxasulfone is the latest Group K herbicide to be released. In Australia, it is registered in bread wheat, triticale, chickpeas, field peas, lentils and lupins for the control of annual grasses and toad rush (*Juncus bufonius*). In North America, it is registered in maize, wheat and soybeans.

There are three chemical classes within the Group K MoA as shown in Table 1. These classes are different types of chemicals; however, they affect the same biochemical pathways in the plant.

Table 1: *Herbicides included in Group K.*

Chemical class	Active ingredient	Product examples
Acetamides	Napropamide	Devrinol®
Chloroacetamides	Dimethenamid	Frontier-P®, Outlook®
	Metolachlor/S-metolachlor	Dual Gold®, Boxer Gold®
	Metazachlor	Butisan®, ClerandaR - metazachlor + imazamox (Gp B)
	Propachlor	Ramrod®
Isoxazoline	Pyroxasulfone	Sakura®

Boxer Gold® contains more than one active constituent.

Source: http://www.croplife.org.au/resistance-strategy/herbicide-mode-of-action-groups/

For more information on plastids, go to: http://www.biologyexams4u.com/2012/06/plastids.html.

2K.1 Mode of action and biochemical pathways

The primary target of the chloroacetamides has not been fully determined. Phytotoxic effects result from membrane disruption. Weeds are killed by severe growth inhibition of seedling shoot and root tissues soon after germination, apparently due to inhibition of cell elongation and cell division. It is also thought that germinating seedlings may not be able to utilise seed reserves. There is evidence that dimethenamid may act on a primary specific target in lipid metabolism. Establishment of seedlings is prevented.

Napropamide inhibits growth by blocking the progression of dividing cells through the cell cycle to mitosis. Reduced rates of cell division and DNA synthesis occur after treatment. This effect may be due to an inhibition in the synthesis or activity of

the cell-cycle-specific proteins. Alpha amylase activity is also inhibited, the extent of which is correlated with the inhibition of tuber germination and subsequent shoot growth in *Cyperus* spp.

Pyroxasulfone inhibits many elongation steps catalysed by the VLCFA elongases.

For detailed explanation, go to Plant & Soil Sciences eLibrary: Inhibitors of fatty acid synthesis and elongation.

2K.2 Absorption into the plant

Germinating grasses are more susceptible when the herbicide is absorbed by the shoot near the coleoptile node. Some herbicide will be absorbed by the roots. Broadleaf (dicot) species absorb chloroacetamides through shoots and roots.

2K.3 Translocation within the plant

Because chloroacetamide herbicides affect plant seedlings soon after germination, translocation is not an important biological property. They are lipophilic (Table 2), and phloem transport is unlikely.

Napropamide is rapidly translocated from the roots to the leaves in broadleaf words; however, there appears to be little movement from roots to shoots in grasses.

Despite pyroxasulfone being readily translocated from roots to shoots, it has no phytotoxic effect in established plants.

Table 2: *Environmental characteristics of Group K herbicides.*

Group K class	Active ingredient	Example trade name	Water solubility (mg/L)	Log K_{ow}	Soil persistence (half-life @ 20°C) (days)	Soil mobility (K_{oc}/K_{foc})	Drift potential (Henry's Law constant, 25°C)
Acetamides	Napropamide	Devrinol®	74	3.3	72	839, slight	Non-volatile
Chloroacetamides	Dimethenamid-p	Outlook®, Frontier-P®	1499	1.89	7	227, moderate	Non-volatile
	S-Metolachlor	Dual Gold®, Boxer Gold PM®	480	3.05	21	226, moderate	Moderate
	Metazachlor	Butisan®	450	2.49	7	54, mobile	Volatile
	Propachlor	Ramrod®	580	1.6	5	80, moderate	Moderate
Isoxazoline	Pyroxasulfone	Sakura®	3.5	2.39	22	233, moderate	Non-volatile

Log K_{ow}, ratio of herbicide that is soluble in octanol (organic solvent) v. water; it is a good indicator of the lipophilic or hydrophilic nature of an herbicide; the larger the log K_{ow} value, the more lipophilic the herbicide; herbicides with values between –1 and 1 should move in the phloem following foliar application. K_{oc}/K_{foc}: >1000 binds strongly to soil; <500, moves in water.

Source: Pesticides Properties Database, http://sitem.herts.ac.uk/aeru/ppdb/en/index.htm

2K.4 Symptoms

With pre-emergent application, the seedlings usually fail to emerge from the soil. Cell elongation slows quickly. Susceptible monocots that do emerge appeared twisted and malformed with leaves tightly rolled in a whorl.

Broadleaf seedlings may have enlarged cotyledons, slightly cupped or crinkled leaves and shortened leaf midribs causing the leaf to look like the mid-vein has been drawn back towards the stem. Leaf colour can be very dark green.

Photo 1: *Wheat damaged with Sakura on the right versus no damage on the left. Note the stunted and thickened coleoptiles, the majority of these plants will fail to emerge.*

Photo: Penny Heuston

Photo 2: *S-metolachlor causing sorghum leaves to tightly roll in a whorl.*

Photo: Mark Congreve, ICAN

Photo 3: *Boxer Gold™ (s-metolachlor + prosulfocarb) stunting on a wheat plant caused by seed being sown too shallow.*

Photo: T. Klein, Syngenta

Photo 4: *A wheat crop with black or wild oats being affected by Sakura (pyroxasulfone) residues in the spray tank.*

Photo: Rural Directions

2K.4.1 Timeframe for symptoms and plant death

Rate of development of symptoms and subsequent damage and death depend on the plant species, herbicide dose, age and size of plant, and rate of plant growth.

2K.5 Crop selectivity

Selectivity of Group K herbicides is a combination of effects including physiological and positional selectivity (Table 3). Differential translocation between species also appears to play a role.

Selectivity of metolachlor and s-metolachlor in maize is due to the size of the germinating seed, position of seed in relation to the herbicide-treated soil, and the ability of the crop to metabolise the herbicide.

Maize cultivars can differ in sensitivity to acetamide herbicides. On light soils and particularly under adverse environmental conditions, phytotoxicity may occur if the herbicide moves into the crop seed zone.

Photo 5: *Maize affected on the right by metolachlor. Grain sorghum seed must be treated with the safener oxabetrinil to speed metabolism of s-metolachlor.*

Photo: NSW DPI

For use in direct-seeded wheat, barley, oats, triticale and canola, s-metolachlor and metolachlor must be applied pre-sowing or the drill-row slot must be closed before spraying.

Table 3: *Differences in efficacy between Group K chemical classes.*

Group K class	Active ingredient	Crops	Weeds
Acetamides	Napropamide	Direct-seeded and transplanted tomatoes, almonds, stone fruit, grapevines	Pre-emergent control of a range of annual grasses and broadleaf weeds
Chloroacetamides	Dimethenamid-p	Field peas, lupins, chickpeas, green beans, navy beans, maize, sweet corn, kabocha squash, pumpkins	Pre-emergent control of a range of broadleaf and grass weeds
		Poppies	Post-emergent control of fumitory in poppies
	Metolachlor/ s-metolachlor	Broccoli, Brussels sprouts, cabbages, cauliflower, sorghum, soybeans, sunflowers, peanuts, maize, sweet corn, sugarcane, potatoes, sweet potatoes, green beans, navy beans, chickpeas, faba beans, field peas, lentils, lupins, tobacco, cotton, canola, wheat, barley, triticale, oats, clover pastures	Pre-emergent control of a wide range of grass and broadleaf weeds and toad rush
	Propachlor	Maize, sweet corn, sorghum, direct-seeded onions; transplanted broccoli, Brussels sprouts, cabbages, cauliflower, Chinese cabbage; beetroot	Pre-emergent control of a range of grass and broadleaf weeds
Isoxazoline	Pyroxasulfone	Bread wheat, triticale, chickpeas, field peas, lentils, lupins	Pre-emergent control of a range of grass weeds and toad rush

MORE INFORMATION

See the comprehensive GRDC Spray Application GrowNote for more information. https://grdc.com.au/Resources/GrowNotes-technical/Spray-Application-Manual

2K.6 Effect of environmental conditions on activity

Group K herbicides are non-ionic and interact with soil organic matter (Figure 1). Metolachlor and s-metolachlor will bind approximately twice as much as pyroxasulfone.

Despite these herbicides having moderate leaching ability, several precautions need to be taken to ensure separation of crop seed from the herbicide.

The dimethenamid label states that it should not be used on soils with a low cation exchange capacity, clay content <10% or organic matter <2%.

S-Metolachlor should not be used on *Brassica* crops when the soil contains >60% sand and silt or is low in organic matter.

Group K herbicides are decomposed by microorganisms once within the soil.

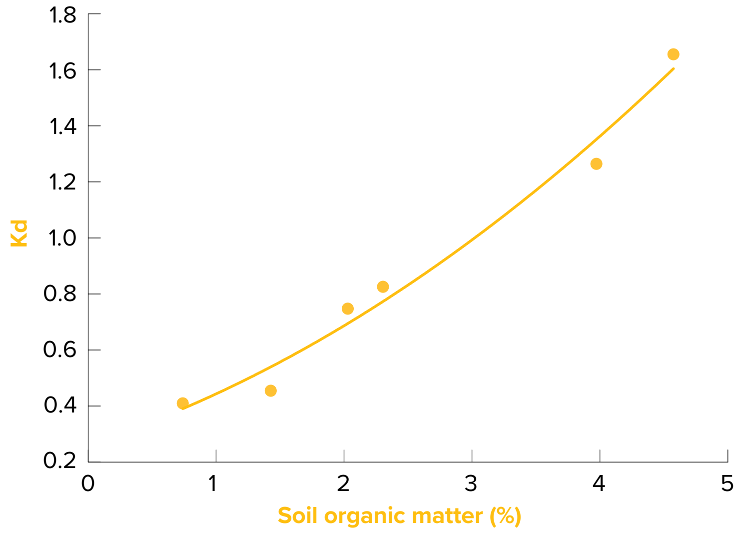

Figure 1: *Relationship between pyroxasulfone binding and organic matter in Australian soils. The higher the soil organic matter, the more the herbicide is bound.*

Source: D Shaner 2013

2K.6.1 Light

Photodegradation is a major path of breakdown of metolachlor, s-metolachlor and napropamide when on the soil surface but plays only a minor role with dimethenamid and pyroxasulfone.

2K.6.2 Temperature

Warmer soil temperatures promote plant growth, which speeds the action of Group K herbicides. Warm, moist soil will also speed the decomposition of these herbicides.

Low soil temperatures will increase the likelihood of crop damage.

2K.6.3 Humidity

Humidity has little effect on the action of these herbicides.

2K.6.4 Soil moisture

Adequate soil moisture is required for Group K herbicides to make contact with roots and shoots via the soil solution and be absorbed. If weeds emerge through dry soil, they will be unaffected by these herbicides.

Waterlogged conditions will increase the likelihood of crop damage.

2K.6.5 Rainfall

These herbicides require irrigation or rainfall to move into the top 50 mm of soil, or light cultivation such as incorporation by sowing. The pyroxasulfone label suggests incorporation within three days of spraying.

Leaching of these products into the crop seed zone is possible in soils of low clay and organic matter.

Group K herbicides intercepted by crop residue will need ~25 mm of rain to move 80% of the herbicide to the soil. S-Metolachlor and metolachlor will volatise from the crop residue.

2K.7 Spray application

Group K herbicides are effective only on germinating seedlings; therefore, even coverage of the soil is important. Even coverage of the soil is particularly important when spraying into crop residues.

These herbicides should be applied as a coarse spray quality with an application volume that gives good crop residue penetration; for example, the Sakura® (pyroxasulfone) label states 50–100 litres per hectare, and Dual Gold® (s-metolachlor) 60 litres per hectare.

Poor control is likely if applied to heavily rilled or excessively cloddy soil.

Pyroxasulfone also has a downwind buffer zone of 80 m where there are ponds, streams and rivers are present.

MORE INFORMATION

See the comprehensive GRDC Spray Application GrowNote for more information.
https://grdc.com.au/Resources/GrowNotes-technical/Spray-Application-Manual

See the GRDC Adjuvants Booklet
https://grdc.com.au/resources-and-publications/all-publications/publications/2015/04/adjuvants-booklet

2K.7.1 Adjuvants

Because Group K herbicides are soil-active, adjuvants are unnecessary unless being tank-mixed with another product.

2K.7.2 Water quality

Water quality is generally not an issue with Group K herbicides. However, it must be taken into account when tank-mixing with another product because water quality may affect the tank-mix partner.

2K.8 Further reading

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Herbicide Group L modes of action

The Group L Mode of Action (MoA) herbicides are also called bipyridyls and photosystem I (PSI) inhibitors. They are classified as Group D by the global Herbicide Resistance Action Committee (HRAC) and Group 22 by the Weed Science Society of America (WSSA) (http://hrac.tsstaging.com/tools/classification-lookup).

There are two herbicides within the Group L MoA: paraquat and diquat (Table 1). Both herbicides are active on grasses and dicot weeds; however, diquat is less effective on grasses.

Table 1: *Herbicides included in Group L.*

Chemical class	Active ingredient	Product examples
Bipyridyls	Paraquat	Gramoxone®, Spray.Seed® (paraquat + diquat), Alliance® (amitrole + paraquat, pre-mix), Para-Trooper (paraquat + amitrole, pre-mix)
	Diquat	Reglone®, Spray.Seed®

Source: http://www.croplife.org.au/resistance-strategy/herbicide-mode-of-action-groups/

Paraquat was commercially released in 1960, with diquat released in 1962.

These herbicides are currently used on at least 140 million hectares globally and ~11 million hectares in Australia. In Australia, paraquat usage has increased dramatically since 2008 because it has been used as the second knock following glyphosate to manage the development of glyphosate resistance in fallows. There are >120 products on the Australian market containing paraquat. Many growers are now using paraquat as a knockdown herbicide in its own right because of the decline in price. Paraquat is also used for 'spray-topping', i.e. using a 'normally sublethal rate', to stop grass seedset selectively from clover pastures in spring and stop the seedset of weeds in pulses before harvest.

Diquat is largely used as a pre-harvest crop desiccant, a knockdown in lucerne and certain horticultural crops, and for weed control in aquatic areas.

2L.1 Mode of action and biochemical pathways

Group L herbicides block photosynthesis at the photosynthetic membrane system PSI, via electron diversion (see box text: What is photosystem I?). This process occurs within the chloroplasts.

2L.1.1 Diversion of electrons in photosystem I

Herbicides such as paraquat and diquat interact with the electron-transfer components associated with PSI. The paraquat ions have a strong positive charge and preferentially attract the free electrons produced by photosynthesis. When the herbicide is 'reduced' by an electron, it rapidly transfers the electron to oxygen, forming highly reactive superoxide including hydrogen peroxide. Chemically highly reactive, these superoxides attack unsaturated membrane fatty acids and chlorophyll, rapidly opening up and disintegrating the cell membranes and tissues. The paraquat acts as a catalyst and the ion–free radical process, then recycles producing further quantities of superoxide until the supply of free electrons ceases.

What is photosystem I (PSI)?

Photosystem I is the second part of the photosynthetic light reaction that occurs within the thylakoid membrane of the chloroplasts. Photosystem II uses light energy to oxidise two molecules of water into one molecule of molecular oxygen. The four electrons removed from the water molecules are transferred by an electron-transport chain through PSI, ultimately to reduce 2NADP$^+$ to 2NADPH.

NADPH is a high-energy electron donor that is used in the Calvin–Benson cycle—the second stage of photosynthesis that takes place in the stroma of the chloroplasts—to reduce phosphoglycerate, producing phosphoglyceraldehyde. These aldehydes are used to create glucose.

The Calvin–Benson cycle can occur without sunlight.

2L.2 Absorption into the plant

Group L herbicides are highly water-soluble and polar (have a strong positive charge). They are rapidly absorbed by green plant tissues and are rain-fast within an hour. They are strongly absorbed to negative leaf surfaces.

A non-ionic surfactant is included in the formulation to ensure low surface tension of the solution and rapid movement through the aqueous pathway.

2L.3 Translocation within the plant

Group L herbicides are rapidly absorbed into the apoplast, including the xylem. They then enter plant cells via the active transport that moves the paraquat or diquat molecule across the cell membrane against its concentration gradient. This type of transport—called active absorption—involves a protein carrier located on the cell membrane that uses energy to move the herbicide from one side of the membrane to the other. The protein carries the molecule into the plant cell, increasing its concentration within the cell to levels well above those outside the cell. Paraquat is transported by the putrescine polyamine carrier.

In the presence of light, the herbicide is rapidly activated within the cells, causing massive damage to cell membranes. This rapid action prevents the translocation from treated leaves.

Application late in the day under low light conditions allows some movement within the xylem before the herbicide is activated by sunlight.

When soils are dry and relative humidity is high, downward movement of paraquat has been observed in potatoes, leading to tuber damage.

For more information on active absorption, go to Plant & Soil Sciences eLibrary: Cellular absorption of herbicides: Active absorption—three herbicide examples.

2L.4 Symptoms

Symptoms vary with plant type, herbicide rate, temperature and humidity.

Small weeds with good spray coverage will begin to wilt within a few hours of application, followed by complete desiccation in one to three days.

Larger plants and/or lower effective doses lead to wilting and interveinal yellowing within a few hours. Leaf edges brown first, followed by desiccation of the whole leaf.

At sublethal rates of herbicide, grasses can exhibit bleaching of new growth with death of older growth. This can be confused with damage from other herbicide MoAs.

Spray drift gives necrotic (brown) spotting on leaves.

YouTube video. Ohio State University Weed Science time lapse of effect of paraquat on giant ragweed.

2L.4.1 Timeframe for symptoms and plant death

Rate of development of symptoms and subsequent damage and death depend on the plant species, herbicide dose, age and size of plant, and rate of plant growth. Death occurs from as early as one day to six days after treatment.

2L.5 Plant selectivity

Despite plants being unable to metabolise paraquat and diquat, there are species differences in efficacy between herbicides. Translocation through the plant is limited by rapid action in the presence of light.

Paraquat is effective on a wide range of species but not effective on capeweed (*Arctotheca calendula*), black bindweed (*Fallopia convolvulus*) and *Erodium* species.

For effective control, grasses must be at least at the Z12 development stage on the Zadoks scale.

Established perennial species will regrow following spraying.

2L.6 Soil activity

Bipyridyl herbicides are irreversibly bound to clay particles and humus, owing to the strong positive charges on the cation. This makes them unavailable for microbial breakdown or leaching (Table 2).

Table 2: *Environmental characteristics of Group L herbicides.*

Active ingredient	Example trade name	Water solubility (mg/L)	Log *Kow*	Persistence in soil (half-life @ 20°C) (years)	Soil mobility (*Koc/Kfoc*)
Paraquat dichloride	Gramoxone®	620,000	–4.5	20	Non-mobile
Diquat dibromide	Reglone®	718,000	–4.6	1–20	Non-mobile

Log Kow, ratio of herbicide that is soluble in octanol (organic solvent) v. water; it is a good indicator of the lipophilic or hydrophilic nature of a herbicide; the larger the log Kow value the more lipophilic the herbicide; herbicides with values between –1 and 1 should move in the phloem following foliar application. Koc/Kfoc >1000 binds strongly to soil, <500 moves in water.

2L.7 Effect of environmental conditions on activity

These herbicides are strongly absorbed by clay colloids. Foliar absorption by the plant is extremely rapid.

2L.7.1 Light

Bipyridyl herbicides are activated by light through the generation of free electrons from photosynthesis.

Application of bipyridyls late in the day has shown modest improvements in herbicide efficacy by allowing more time for translocation within the plant.

In a trial in the USA, desiccation of cotton at days 3 and 14 after treatment was much better from evening applications than from morning and midday applications.

Failed maize stands were better controlled when a paraquat + Group C herbicide mix was applied at sunset than at sunrise.

In Australia, a trial comparing night and day paraquat applications for control of large awnless barnyard grass in fallow found that three litres per hectare (L/ha) applied at night was equivalent to 6 L/ha during the day (Table 3).

Table 3: *Effect of a single application of paraquat on large awnless barnyard grass plants (BYG) at day 24 after treatment.*

Paraquat treatment	BYG alive per plot (2 m × 10 m)	
	Day	Night
Untreated	210	
2 L/ha	46	19
3 L/ha	59	14
6 L/ha	12	0

Source: Cook et al. 2015

Some photodegradation takes place on desiccated leaf surfaces and surface soil. This is estimated at 25–50% of the total applied over three weeks of strong light, but has not been unequivocally determined in the field.

2L.7.2 Temperature

As temperature increases, the rate of uptake of herbicide increases provided respiration and photosynthesis are not limited by the conditions. However, the total amount of herbicide absorbed does not change.

Higher temperatures increase the rate of photosynthesis; therefore, a greater quantity of reactive oxides will be produced, shortening the time for symptoms to develop.

2L.7.3 Humidity

High humidity increases the lifespan of hydrated droplets of Group L herbicides on the leaf surface. High humidity also makes the aqueous pathway through the cuticle more permeable to polar herbicides such as the bipyridyls.

Plants growing under high humidity also have thinner cuticles and are generally easier to control.

As noted previously, high humidity along with low soil moisture increases the downward movement of paraquat from the leaves to the tubers of potatoes during pre-harvest desiccation.

2L.7.4 Soil moisture stress

Stressed plants have thicker cuticles, which will increase the length of the aqueous path accessed by Group L herbicides. The additional waxes or hairs can increase herbicide runoff and droplet bounce, reducing herbicide coverage.

Moisture stress means lower rates of photosynthesis; therefore, fewer free electrons will be available for oxygen radicals.

2L.7.5 Rainfall

Group L herbicides are rain-fast anywhere between 15 minutes and two hours. Therefore, rain following application will have little effect on application.

2L.8 Spray application

Group L herbicides are poorly translocated within the plant because of their rapid action, so spray coverage is critical. Spray target should be at least 15% coverage.

Label recommendations vary from specifying a minimum application volume of 50 L/ha to 100–150 L/ha. Most Australian growers will now have a minimum application volume of 70 L/ha.

No spray-quality recommendation is listed on labels. Generally, however, a medium to coarse spray quality would be recommended, with increasing application volume as spray quality becomes coarser.

2L.8.1 Adjuvants

Additional wetting agents are not required with lower concentration products (e.g. 250 g/L) unless high-volume spraying results in excessive dilution of the wetter (i.e. <400 mL per 100 L spray volume) or for the control of certain species.

Higher concentration products such a Gramoxone® 360 always require additional adjuvant because there is less in the formulation.

Read the label for recommended use of adjuvants.

2L.8.2 Water quality

Bipyridyl herbicides are not affected by most of the water-quality problems that affect weak acid herbicides.

Temperature

No data is available on the effect of low spray-solution temperatures on efficacy.

pH

Bipyridyl herbicides are stable in acid–neutral pH solutions but unstable in alkaline solutions.

Do not leave spray mixed overnight.

Hardness

Hardness has no effect on bipyridyls herbicides.

Turbidity

Water containing clay, silt or algae is unsuitable for using with bipyridyls herbicides. These herbicides bind tightly to soil particles and organic matter.

Water that has contains these impurities should be stored in settling tanks and filtered before use.

Low levels of turbidity can be overcome by using higher label rates and the lower end of application volumes.

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Herbicide Group M modes of action

The Group M Mode of Action (MoA) herbicides are glycines and are represented by the single herbicide glyphosate. Glyphosate is classified as Group G by the global Herbicide Resistance Action Committee (HRAC) and Group 9 by the Weed Science Society of America (WSSA) (http://hrac.tsstaging.com/tools/classification-lookup).

Glyphosate is a non-selective herbicide, active against most grass, other monocot (e.g. sedges and lilies) and dicot species, although it is most effective on grasses.

Glyphosate is the most widely used herbicide in the world, with annual global sales of more than $6 billion, exceeding the combined sales of the next 10 most used crop-protection products. To allow over-the-top crop spraying of glyphosate, resistance genes have been introduced to cultivars of maize, soybean, cotton, lucerne, canola, sugar beet, tobacco, tomato, chicory, carrots and petunias.

2M.1 Biochemical pathway

Glyphosate blocks the shikimate biosynthetic pathway by binding to 5-enolypyruvyl-shikimate-3-phosphate (EPSP) synthase (Figure 1). The shikimate pathway produces the three key aromatic amino acids tryptophan, tyrosine and phenylalanine, which are essential for the production of auxins, phytoalexins, folic acid, lignin, plastoquinones and other secondary products required to fix carbon for plant growth. [1]

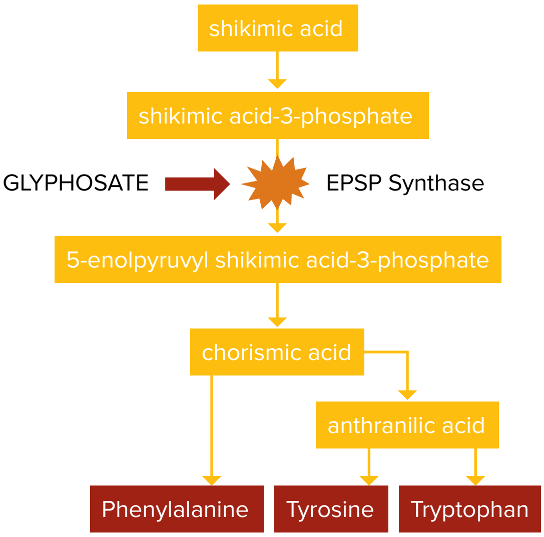

Figure 1: *The shikimate pathway.*

Blocking the shikimate pathway leads to a reduction in sugar production and a buildup of toxic products such as shikimate. [2]

The shikimate pathway occurs in the chloroplasts in the leaves and, importantly, in the meristematic regions of the plant (tips of roots, shoots and cambium) where cell

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[1] D Shaner (2006) An overview of glyphosate mode of action: Why is it such a great herbicide? North central Weed Science Society Proceedings, http://ncwss.org/proceed/2006/abstracts/94.pdf

[2] L Hall *et al.* (1999) How herbicides work. Biology to Application. Alberta Agriculture and Rural Development, http://www1.agric.gov.ab.ca/$Department/deptdocs.nsf/all/agdex33/$FILE/606-2.pdf

division is occurring. After absorption, glyphosate translocates to these meristematic regions, to which the products of photosynthesis are also moved (carbon sinks).

The shikimate pathway occurs in plants, fungi, bacteria and many other single celled organisms but not in animals; hence, glyphosate has low toxicity to vertebrate and invertebrate animal species.

2M.2 Absorption into the plant

Glyphosate penetrates the leaf through the spaces in the leaf cuticle (aqueous pathway) then the epidermis by diffusion. The rate of penetration is determined by herbicide formulation, herbicide rate (concentration of herbicide in droplet), adjuvants and environmental conditions.

Water solubility of glyphosate is affected by the pH of the solution, temperature and formulation (Table 1). Glyphosate acid has a relatively low water solubility. To improve its uptake by increasing its solubility, it is formulated as a salt (isopropylamine, di-ammonium, mono-ammonium or potassium).

When formulated as a salt, glyphosate is able to enter the leaf via the cuticle and epidermis quite easily in most plant species. Species with excessively hairy or waxy leaves often require higher application rates to achieve control, most likely due to reduced penetration of the leaf surface.

Dust on the leaves will absorb glyphosate and prevent it from passing the through the cuticle and epidermis.

Table 1: *Environmental characteristics of Group M herbicides.*

Group M class	Active ingredient	Example trade name	Water solubility (mg/L)	Log *K*ow	Persistence in soil (half-life @ 20°C) (days)	Soil mobility (*K*oc/*K*foc)
Glycines	Glyphosate acid	Technical grade, not sold as a herbicide	15,700 at pH 7 11,600 at pH 2.5	0.0006–0.0017	24	20,870, non-mobile
	Glyphosate isopropylamine	Roundup® CT	900,000 at pH 7 786,000 at pH 4			
	Glyphosate trimesium salt	Touchdown® Broadacre	4,300,000 at pH 7			

Log Kow is the ratio of herbicide that is soluble in octanol (organic solvent) v. water. It is a good indicator of the lipophilic or hydrophilic nature of a herbicide; larger the log Kow value the more lipophilic the herbicide; herbicides with values between –1 and 1 should move in the phloem following foliar application. Koc/Kfoc: >1000, binds strongly to soil; <500, moves in water. Solubility will vary with temperature and pH.

2M.2.1 Cellular absorption: passive diffusion and active absorption

The most common type of cellular absorption is passive, whereby the herbicide moves freely from an area of higher concentration in the symplast to an area of lower concentration in the cell, requiring no input of energy. (Refer to text box in Herbicide GrowNote: Group A for explanation of symplastic movement.)

Glyphosate can also be absorbed into plant cells via active absorption, which moves the herbicide molecule across the cell membrane against the concentration gradient. This increases the concentration of herbicide within the cell and it is facilitated by a protein carrier located in the cell membrane.

For a detailed explanation of this process, go to University of Nebraska Plant & Soil Science e-Library: Cellular absorption of herbicides—active absorption, general concepts.

2M.3 Translocation within the plant

Glyphosate is a relatively small molecule and is a weak acid herbicide so is readily translocated from the leaves to the growing tips (meristematic regions) of the shoots and roots. Up to 70% of absorbed glyphosate translocates away from the leaves but this occurs for only the first 48–72 hours after application. [3]

Glyphosate primarily translocates basipetally in the plant (i.e. from the leaves to the roots) in association with sugars moving in the phloem. Glyphosate affects the carbon flow in the chloroplasts, ultimately reducing sugar production and movement of glyphosate in the phloem. (For more information on chloroplasts, see: How herbicides work. Biology to application, p. 53.) [4]

Glyphosate is poor at killing small grasses. Very small (one-leaf) grasses are still growing on seed reserves and have not commenced sugar production via photosynthesis. This means little downward flow of sugars and glyphosate, ultimately leading to less reliable control. Glyphosate accumulates in the leaf tip and not the meristem in these small grasses. [5]

2M.4 Timing of the double-knock

A double-knock is the sequential application of two weed control tactics applied in such a way that the second tactic controls any survivors of the first tactic. A common combination is glyphosate followed by paraquat or paraquat/diquat. The technique is primarily a herbicide-resistance management tool to minimise the chance of survival from the first control treatment (knock).

When glyphosate is the first knock, three to seven days should be allowed before the second knock is conducted. This allows sufficient time for glyphosate to translocate to the meristems in the shoots and roots. On-label rates should be used for both herbicides.

To allow translocation of glyphosate to the root systems of large plants and perennial species, the second knock should be delayed at least seven days.

For more information, see GRDC IWM manual for Australian Cropping systems. Section 4. Tactics for managing weed populations (pp. 128–132). [6]

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[3] D Shaner (2006) An overview of glyphosate mode of action: Why is it such a great herbicide? North central Weed Science Society Proceedings, http://ncwss.org/proceed/2006/abstracts/94.pdf

[4] L Hall *et al.* (1999) 'How herbicides work. Biology to application.' Alberta Agriculture and Rural Development, http://www1.agric.gov.ab.ca/$Department/deptdocs.nsf/all/agdex33/$FILE/606-2.pdf

[5] Roundup Ready Flex Cotton technical manual. Monsanto, http://www.monsanto.com/global/au/products/documents/roundup-ready-flex-technical-manual.pdf

[6] L Hall *et al.* (1999) 'How herbicides work. Biology to application.' Alberta Agriculture and Rural Development, http://www1.agric.gov.ab.ca/$Department/deptdocs.nsf/all/agdex33/$FILE/606-2.pdf

2M.5 Symptoms

The first symptom of glyphosate application is wilting of the target plant. This is transient and is followed by chlorosis (pale yellow-green coloration) of the growing points and the new, expanding leaves. Chlorosis spreads throughout the plant, followed by necrosis (cell death) and the final death of the plant. Chlorosis and necrosis in some species are associated with an increase in tissue anthocyanins, which gives the plant a red coloration.

Sublethal glyphosate rates slow vegetative growth. New growth may appear bleached (white longitudinal striping in grasses) and is often deformed (downward bending 'epinastic' growth). Often there are multiple new deformed shoots and roots produced, and this can be mistaken for phenoxy herbicide damage. In large or perennial weeds, regrowth can occur after an initial brownout, often at the epicormic buds on the stems and trunks.

Photo 1: *Dead wheat plants on the right versus a severely affected, multi-tillered plant on the left from glyphosate.*

Photo: Tim McNee, NSW DPI

Photo 2: *Bleached new growth from a sub-lethal rate of glyphosate on soybeans.*

Photo: DPI&F

Photo 3: *Multiple new deformed shoots on wheat plants from a sub-lethal rate of glyphosate.*

Photo: Tim McNee, NSW DPI

2M.5.1 Timeframe for symptoms and plant death

Rapidity of symptoms is determined by herbicide rate, plant susceptibility and size, and environmental conditions. Wilting occurs in first 24 hours, from which plants then recover. This is often missed by observers.

Under ideal conditions of warm temperatures, good soil moisture, small plants and high humidity, the first signs of leaf chlorosis on sensitive weed species may be evident within four–five days after application. In many instances, symptoms take 10–21 days to appear.

Where weeds are larger and/or more tolerant or where plant metabolism is slowed by cold temperatures, waterlogging or moisture stress, symptoms will appear much later. Older or larger plants have more stored reserves, which need to be run down before chlorosis will be evident. Woody perennials may take weeks or even months to begin to express chlorosis and subsequent leaf loss.

2M.6 Plant selectivity

Glyphosate is classified as a non-selective herbicide. This broad spectrum of weed control occurs because most plants have a common shikimate pathway and EPSP synthase binding site, coupled with no ability to metabolise glyphosate rapidly.

Glyphosate resistance has been introduced into crop species by inserting genes from bacteria that enable metabolism of glyphosate by the plant.

2M.7 Soil activity

Glyphosate has a typical field-soil half-life of 24 days (Table 1). This indicates moderate persistence in the soil, with soil breakdown occurring slowly via microbial degradation. However, glyphosate binds quickly and very tightly to the lattice structure of clay particles. This strong binding prevents uptake of glyphosate by germinating or emerging seedlings, or by roots of existing plants.

Strong binding to soil also usually prevents leaching and/or runoff.

Instances of plant damage caused by glyphosate residues have been recorded in soils with very low clay and organic matter content, but are uncommon.

2M.7.1 Breakdown pathways

Microbial degradation is the major pathway of glyphosate breakdown in the soil. The rate of degradation varies depending on the soil texture, temperature and moisture.

Because there is negligible degradation of glyphosate within the plant, late-season applications for weed control or crop desiccation close to harvest can give detectable residues on straw and possibly in grain. When glyphosate is used close to harvest, it is therefore critical that label recommendations are followed, to ensure that maximum residue limits (MRLs) are not exceeded.

2M.8 Effect of environmental conditions on activity

Any environmental variable that affects plant growth will affect the translocation and efficacy of glyphosate. For example, drought stress was shown to reduce the efficacy of glyphosate by two to eight times on velvetleaf (*Abutilon theophrasti*). [7] The efficacy of low or marginal rates of herbicide can be greatly influenced by environmental conditions. Use of robust rates is the best way to reduce the influence of environmental variability on weed control.

2M.8.1 Light

Light drives photosynthesis and therefore has a major effect on plant growth and development. High intensity of light can also increase the amount and type of wax in the leaf cuticle.

High intensities of light (common in Australia) will increase the rate of uptake and translocation of glyphosate. However, the total amount of herbicide translocated is likely to be the same as for lower light intensity. High intensities of light also speed the rate of symptom development.

The time of day at which glyphosate is applied can have varying influences on glyphosate efficacy.

Some research has shown that glyphosate interception and control in dicot species with diurnal leaf movement is reduced with night spraying as the weed leaves become more vertical. However, this change in leaf orientation at night only explained some of the difference in levels of control. [8] [9]

Some have postulated that night spraying reduces control because photosynthesis and the production of sugars cease, affecting translocation. [10]

On the other hand, two separate research projects conducted in Western Australia investigating the control of the summer growing weed button grass (*Dactyloctenium radulans*) found little difference in level of control between night and day spraying. Increasing glyphosate rate and application volume made the greatest improvements in control. [11] [12]

2M.8.2 Temperature

The rate of absorption and translocation of glyphosate increases with temperature provided photosynthesis and transpiration are not limiting.

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[7] J Zhou *et al.* (2007) Glyphosate efficacy on velvetleaf (*Abutilon theophrasti*) is affected by stress. *Weed Science* 55, 240–244, http://www.bioone.org/doi/abs/10.1614/WS-06-173.1?journalCode=wees

[8] K Mohr *et al.* (2007) Application time of day influences glyphosate efficacy. *Weed Technology* 21, 7-13, https://www.jstor.org/stable/4495801?seq=1#page_scan_tab_contents

[9] JK Norsworthy *et al.* (1999) Diurnal leaf movement effects on spray interception and glyphosate efficacy. *Weed Technology*, 466-470, https://www.jstor.org/stable/3989032?seq=1#page_scan_tab_contents

[10] AL Waltz *et al.* (2004) Glyphosate efficacy on velvetleaf varies with application time of day 1. *Weed Technology* 18, 931-939, http://digitalcommons.unl.edu/cgi/viewcontent.cgi?article=1419&context=agronomyfacpub

[11] G Thompson (2011) Controlling button grass in summer with herbicides. North East Farming Futures, http://www.cropcircleconsulting.com.au/images/userfiles/file/Evaluation%20of%20herbicides%20to%20control%20BUTTON%20GRASS%202011%20NEFF.pdf

[12] A Hashem, M Amjad (2016) Controlling button grass (*Dactyloctenium radulans*): an emerging summer weed in the northern agricultural region of Western Australian wheatbelt. 2016 GRDC Grains Research Updates, Perth, http://www.giwa.org.au/2016researchupdates

Species that can metabolise glyphosate, such as enhanced-metabolism resistant weed biotypes, will show higher levels of control at lower temperatures than at higher temperatures due to slower breakdown of the herbicide. [13] However, research on glyphosate-resistant and -susceptible populations of awnless barnyard grass (*Echinochloa colona*) at the three–four-leaf stage found better control of both biotypes with the full label rate of glyphosate at day–night temperatures of 25°–20°C than 35°–30°C, at ~75% relative humidity for both treatments. [14] This could be due to a range of factors including increased or different wax deposits on the leaves of plants grown at higher temperatures and possibly greater upward movement of glyphosate in the xylem with increased transpiration by the plant moving the herbicide away from the meristems.

2M.8.3 Humidity

Lower humidity increases the speed of droplet drying, meaning less time for glyphosate to be absorbed, because absorption ceases when the deposit dries (see *Adjuvants* below).

A full wetted cuticle will favour the penetration of water-soluble herbicides such as glyphosate. Low humidity is likely to increase plant transpiration, assuming soil moisture is adequate, increasing the upward movement of glyphosate in the xylem and reducing movement towards growing points in roots and rhizomes.

2M.8.4 Soil moisture stress

Low availability of soil moisture reduces the effectiveness of glyphosate through reduced translocation and photosynthesis. Moisture-stressed plants can also have smaller leaves, thicker cuticles and more wax deposits, reducing the effective target area and glyphosate absorption.

Research in northern New South Wales investigating the interaction in awnless barnyard grass between moisture stress and glyphosate efficacy showed that large plants needed higher rates of glyphosate. Control was improved when rain occurred prior to rather than after spraying. [15]

2M.8.5 Rainfall

Rainfall prior to herbicide application affects available soil moisture as well as reducing the amount of crystalline wax on leaves. Rainfall prior to spraying will also wash off dust from the leaves. Dust on the leaves can absorb glyphosate and prevent it from passing the through the cuticle and epidermis.

Rain shortly after glyphosate application will wash the herbicide off the leaves because it is hydrophilic. Rain-fast periods stated on labels vary between three and six hours, depending on the glyphosate formulation. The shorter rain-fast periods claimed on some labels are due to smaller glyphosate salt molecules and other premix adjuvants.

Research in northern New South Wales showed a strong link between glyphosate rate and rain-fast period. The higher the glyphosate rate the shorter the effective period for controlling seedling awnless barnyard grass, probably because of faster absorption of the higher concentrations of glyphosate. [16]

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[13] J Zhou *et al.* (2007) Glyphosate efficacy on velvetleaf (*Abutilon theophrasti*) is affected by stress. *Weed Science* 55, 240–244, http://www.bioone.org/doi/abs/10.1614/WS-06-173.1?journalCode=wees

[14] H Han *et al.* (2016) Target-site *EPSPS Pro-106* mutations: sufficient to endow glyphosate resistance in polyploid *Echinochloa colona*? *Pest Management Science* 72, 264–271, https://www.ncbi.nlm.nih.gov/pubmed/25969123

[15] CA Wicks *et al.* (1993) Effect of rainfall on glyphosate performance on stressed grass weeds following wheat harvest. *Plant Protection Quarterly* 8, 2–6.

[16] CA Wicks *et al.* (1993) Effect of rainfall on glyphosate performance on stressed grass weeds following wheat harvest. *Plant Protection Quarterly* 8, 2–6.

2M.9 Spray application

Glyphosate has an optimum spray-application volume of 50–80 litres per hectare and it should be applied as a coarse, or very coarse, spray quality. (Note, however, that label recommendations vary.) Lower application volumes reduce the potential coverage whereas higher application volumes reduce the herbicide concentration in the solution, reducing the speed of absorption.

Because glyphosate is well translocated, the area of spray coverage can be as little as 6–8% as measured with water-sensitive paper.

2M.9.1 Water quality

pH

Glyphosate is a weak acid (pH 4.5–5). When added to the spray tank, glyphosate molecules break apart (disassociate) into negatively charged glyphosate ions, having given up hydrogen (H+) ions and lowering the pH of the spray solution.

NOTE: Test the pH of the water before considering lowering the pH of the spray solution; also test the pH of the spray following addition of the glyphosate. The optimum pH of the spray solution for glyphosate efficacy is 4.5–5.8.

However, reducing the pH of a spray solution is not recommended. Larger gains can be obtained by managing water hardness, increasing the glyphosate rate and ensuring a minimum coverage of 6%.

Water hardness

Hard water contains high levels of calcium, magnesium, bicarbonate, iron, zinc and aluminium cations. Hard water is most commonly defined as containing >150 mg/L (ppm) of calcium carbonate (CaCO3). Using hard water reduces glyphosate efficacy because these cations bind to the negatively charged glyphosate ions. This in turn reduces the herbicide's solubility, reducing leaf penetration. In extreme cases, it can cause the herbicide to precipitate and become sludge on the bottom of the spray tank. [17]

Addition of ammonium sulfate to the spray solution prior to the addition of glyphosate will cause preferential binding between the cations in the water and the negatively charged sulfate ions in the ammonium sulfate, causing them to precipitate. This reduces subsequent binding with glyphosate.

Addition of ammonium sulfate also reduces (but does not eliminate) antagonism between glyphosate and some other herbicides such as triazines.

Suspended particles

Strong binding of glyphosate to clay particles leads to poor herbicide performance either through contamination of spray water or as dust on leaves. Dirty spray water containing suspended clay or organic material will bind and deactivate glyphosate.

As a rule-of-thumb, fill a 10-litre bucket with the water to be used, and place a coin on the bottom of the bucket. If the coin cannot be easily seen, the water is too dirty to use.

Spraying in dusty conditions can also deactivate glyphosate. This is a particular problem in lighter soil types prone to dust, and especially around the wheels tracks of sprayers (Photo 4).

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[17] S McDougall (2012) Water quality for chemical spraying. Primefact. NSW Department of Primary Industries, http://www.dpi.nsw.gov.au/__data/assets/pdf_file/0008/433691/Water-quality-for-chemical-spraying.pdf

Photo 4: *Poor barnyard grass control in wheel tracks, most likely arising from dust at application, probably in association with early onset of moisture stress in compacted wheel tracks and poor coverage.*

Photo: Mark Congreve

Water temperature

Low water temperatures can seriously affect tank mixes containing glyphosate, particularly if the pH of the mix is <5. Pesticides in the tank will come out of solution and form sludge in the sprayer.

There is also some evidence that cold water (~5°C) can reduce the efficacy of glyphosate.

2M.9.2 Adjuvants

The use of some adjuvants with glyphosate can increase the droplet spread and contact with the leaf surface. Other adjuvants can also reduce the speed of droplet evaporation on the leaf surface, thus allowing increased time for penetration.

Always read the product label.

The type, dose and combination of adjuvants used can have a significant impact on efficacy. Some 'premium' glyphosate formulations are loaded with a complete adjuvant 'package' and have no, or minimal, need for additional adjuvants. Other formulations, such as the popular 'CT' isopropylamine salt, are formulated with a minimal quantity of adjuvant and the label requires additional amounts of adjuvant depending on herbicide rate and carrier volume.

Oils are not generally recommended for use with glyphosate when controlling grasses because they can reduce the efficacy.

In summer, however, spray oils can reduce spray droplet evaporation and assist the efficacy of the partner herbicides in a tank mix. For example, potential tank-mix partners for glyphosate that benefit from the addition of spray oil include:

- triclopyr or 2,4-D for control of melons in fallow
- Group G herbicides such as Sharpen® (saflufenacil) in fallow and Valor® (flumioxazin) prior to sowing particular crops
- Group A grass-selective herbicides when used in glyphosate-tolerant canola or cotton.

Strategies to overcome potential antagonism between glyphosate and the spray oil when mixing with partner herbicide include:

- increasing the rate of glyphosate and ensuring optimum coverage

- applying the herbicides separately, the glyphosate first followed by the other herbicide four or five days later.

Typically, 2,4-D ester formulations are compatible with glyphosate. However, 2,4-D amine formulations require careful attention. Similar glyphosate and 2,4-D amine formulations will be compatible, e.g. glyphosate IPA and 2,4-D IPA formulations, but different amine formulations may not be compatible especially when using low spray volumes (higher concentrations of herbicides). This can reduce efficacy and may form precipitates that block nozzles. Combinations that often precipitate are potassium (K salt) and isopropylamine (CT) formulations of glyphosate with 2,4-D DMA formulations.

2M.10 Further reading

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Herbicide Group N modes of action

The Group N Mode of Action (MoA) contains one phosphinic acid herbicide, glufosinate, an inhibitor of glutamine synthase (Table 1).

Glufosinate is classified as Group H by the global Herbicide Resistance Action Committee (HRAC) and Group 10 by the Weed Science Society of America (WSSA) (http://hrac.tsstaging.com/tools/classification-lookup).

Glufosinate is a non-selective, contact-type herbicide that is active on both dicot and monocot weeds and grasses. It is, however, less effective on grasses and perennial species than on broadleaf annual weeds.

Table 1: *Herbicide included in Group N.*

Chemical class	Active ingredient	Product examples
Phosphinic acid	Glufosinate ammonium	Basta®, Liberty® 200

Source: http://www.croplife.org.au/resistance-strategy/herbicide-mode-of-action-groups/

Glufosinate was first commercially released in 1995 and was first discovered in species of *Streptomyces* bacteria.

Glufosinate is used as a knockdown herbicide in orchards, plantations and crops as well as in non-agricultural areas.

Glufosinate-resistance genes originally extracted from two species of *Streptomyces* bacteria have been incorporated into maize, cotton, soybeans, sugar beet and canola. This Bayer-owned trait is called LibertyLink™ and the technology was developed by Bayer CropScience. Bayer estimates 24.3 million hectares of LibertyLink™ crops are being grown annually worldwide.

2N.1 Mode of action and biochemical pathways

Glufosinate irreversibly binds to the enzyme glutamine synthase, which is responsible for combining ammonia (NH3) and glutamate to form glutamine. Glutamine is used in the production of amino acids. Glutamine synthase also recycles ammonia produced by other biochemical pathways within the plant.

The binding to glutamine synthase is followed by a rapid accumulation of ammonia within the plant along with glyoxylate. Glyoxylate is an inhibitor of the RuBisCO enzyme, a key component in the non-light-mediated part of photosynthesis. This blocks photosynthesis and causes a build-up of toxic oxygen radicals.

This process occurs within the chloroplasts.

2N.2 Absorption into the plant

Glufosinate is a highly water-soluble, weak acid herbicide. It is therefore absorbed through leaves and other green tissue via the aqueous pathway through the cuticle and epidermis.

A non-ionic surfactant is included in the formulation to ensure low surface tension of the solution and rapid movement through the aqueous pathway.

Most of the herbicide is absorbed within 72 hours. Temperature has no effect on the total amount of herbicide absorbed.

2N.3 Translocation within the plant

Glufosinate limits its own translocation due the rapid cessation in photosynthesis and cellular destruction following absorption. It is rapidly absorbed into the apoplast, including the xylem, and the symplast, including the phloem.

Translocation rate varies with weed species and growing conditions. Phloem mobility is reduced and xylem transport enhanced in cooler temperatures. This in turn reduces the amount of herbicide being translocated to the meristems, which can then allow regrowth. In addition, less ammonia is produced at lower temperatures.

2N.4 Symptoms and timeframe for symptoms and plant death

VIDEO

Ohio State University Weed Science: Time lapse of effect of glufosinate on velvetleaf.

Symptoms vary with plant type, herbicide rate, temperature and humidity.

Usually, the first symptom is a faint green discoloration on the leaves at ~24–48 hours post-application, associated with a rapid rise in plant-tissue ammonia levels over this time.

In less susceptible species, or at lower effective herbicide rates and lower temperatures, symptoms of leaf-tip burning, tip curling and patchy yellowing will occur over 7–10 days.

Small susceptible weeds exposed to good spray coverage will develop even yellowing of the leaves within 3–7 days followed by complete desiccation in 10–15 days. Under cool conditions, desiccation may take up to 30 days.

Symptoms develop much faster with high light intensity, temperatures >20°C but <33°C, and relative humidity >50%.

If plant meristems remain green, the plant will re-grow.

Photo 1: *Glufosinate effects on oat plants 11 days after treatment.*

Photo: Andrew Storrie, Agronomo

Photo 2: *Glufosinate chlorosis and necrosis on oat plants 5 days after treatment.*

Photo: Andrew Storrie, Agronomo

2N.5 Plant selectivity

Differences in tolerance between weed species have been found to be as high as 70-fold. This appears to be due to differences in:

- rate and extent of herbicide uptake
- translocation within the plant—differences in partitioning of the herbicide between the phloem and the xylem
- capacity to detoxify the herbicide.

All species are more susceptible at higher temperatures (i.e. 30°C > 20°C > 10°C), and when the relative humidity is >50%.

There are differences in susceptibility within grasses, non-grass monocots and broadleaf species.

Grasses tend to need higher rates than broadleaf weeds to achieve control.

Age of the plant will influence rates of herbicide absorption because of thickness and permeability of cuticles.

2N.6 Soil activity

Despite being highly water-soluble, little glufosinate is absorbed by roots, owing to rapid microbial degradation (Table 2).

Soil sterilisation will result in soil activity, with potential damage to the crop.

Glufosinate remains active on inert surfaces such as plastic mulch and it can be later washed off, causing damage to crops.

Table 2: *Environmental characteristics of the Group N herbicide, phosphinic acid.*

Active ingredient	Example trade name	Water solubility	Log Kow	Persistence in soil (half-life @ 20°C)	Soil mobility
Glufosinate ammonium	Basta®	1,370,000 mg/L	–4.6	7 days	Slightly mobile

Log Kow, ratio of herbicide that is soluble in octanol (organic solvent) v. water; it is a good indicator of the lipophilic or hydrophilic nature of a herbicide; the larger the log Kow value the more lipophilic the herbicide; herbicides with values between –1 and 1 should move in the phloem following foliar application.

2N.7 Effect of environmental conditions on activity

2N.7.1 Light

Efficacy of glufosinate increases with increasing light intensity, due to increased photosynthesis.

2N.7.2 Temperature

As temperature increases, the rate of uptake of herbicide increases provided respiration and photosynthesis are not limited by the conditions. However, the total amount of herbicide absorbed does not change.

Higher temperatures increase the rate of photosynthesis; therefore, a greater amount of reactive oxides will be produced, shortening the time for symptoms to develop.

2N.7.3 Humidity

Glufosinate has optimum efficacy when relative humidity is at least 50%. Humidity increases the lifespan of hydrated droplets of Group N herbicide on the leaf surface.

High humidity also makes the aqueous pathway through the cuticle more permeable to water-soluble herbicides.

In addition, plants growing under high humidity have thinner cuticles and are generally easier to control.

2N.7.4 Soil moisture stress

Stressed plants have thicker cuticles, which will increase the length of the aqueous path accessed by Group N herbicide. The additional waxes or hairs can increase herbicide runoff and droplet bounce, reducing herbicide coverage.

Moisture stress means lower rates of photosynthesis; therefore, fewer free electrons will be available for oxygen radicals.

2N.7.5 Rainfall

Glufosinate is rain-fast for six hours.

Because glufosinate is stable on surfaces such as plastic it can be washed off in rain and damage plants that it contacts.

2N.8 Spray application

Glufosinate is poorly translocated within the plant owing to its rapid action, so spray coverage is critical. The spray target should be at least 15% coverage.

Label recommendations are 100 litres per hectare (L/ha) for fallow. A medium spray quality is recommended. For orchards, plantations, vineyards, sugarcane, other row crops, non-agricultural areas, etc., the Basta® label states 300–500 L/ha applied by boom, shielded/hooded or directed spray.

MORE INFORMATION

See the GRDC Adjuvants Booklet https://grdc.com.au/resources-and-publications/all-publications/publications/2015/04/adjuvants-booklet

GRDC Fact Sheet Water quality for spraying operations

2N.8.1 Adjuvants

Glufosinate contains a pre-formulated wetter, and additional surfactant is required only when application volumes are >500 L/ha, or when pines (*Pinus* spp.) are the target species.

Read the label for recommended use of adjuvants.

2N.8.2 Water quality

The label recommends the use of clean water.

pH

Glufosinate is a weak acid herbicide, so will lower the pH of the spray solution when added to the tank. Avoid water with pH ≥8.

Hardness

Water with high levels of cations and bicarbonate should be avoided. Typically, water hardness above 250 to 350ppm ($CaCO_3$ equivalents) should be treated before using herbicides.

Turbidity

Low levels of turbidity will not interfere with the efficacy of glufosinate.

2N.9 Further reading

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Herbicide Group Q modes of action

The Group Q Mode of Action (MoA) herbicides inhibit cyclisation of carotenoids, blocking the formation of xanthophylls. Xanthophyll carotenoids are important in buffering the energy from light reactions in photosynthesis. Symptoms include the bleaching of new growth.

Group Q herbicides are classified as Group 11 by the global Herbicide Resistance Action Committee (HRAC) and Group F3 by the Weed Science Society of America (WSSA) (http://hrac.tsstaging.com/tools/classification-lookup).

There are two chemical classes within the Group Q MoA as shown in Table 1. These classes are different types of chemicals; however, they affect the same biochemical pathways in the plant.

Table 1: *Herbicides included in Group Q.*

Chemical class	Active ingredient	Product examples
Isoxazolidinones	Clomazone	Magister®, Director® 480
Triazoles	Amitrole	Amitrole T, Amitrole 250, Alliance®, Para-Trooper (PM)

Alliance® and Para-Trooper contain more than one active constituent.

Source: http://www.croplife.org.au/resistance-strategy/herbicide-mode-of-action-groups/

Amitrole was the first synthetic, non-selective herbicide produced, being commercialised in 1959. Clomazone was commercialised around 1985.

Amitrole is often formulated with ammonium thiocyanate, which reduces its degradation within the plant. Use of amitrole declined with the introduction of glyphosate; however, it has come back into favour because of the increasing number of glyphosate-resistant weed populations. It is now used in combinations with paraquat and other herbicides to control weeds in fallows, on roadsides, and in other non-crop areas.

In Australia, clomazone is used to control annual grasses in rice crops. It is also registered for use in cucurbits, beans, poppies, potatoes and tobacco. In North America and Europe, clomazone is used in crops of soybeans, cotton, vegetables and sugarcane.

2Q.1 Mode of action and biochemical pathways

Clomazone is metabolised to the active 5-keto form in the plant. This form then blocks deoxyxylulose 5-phosphate synthase, a key enzyme of plastid isoprenoid synthesis, at the start of the pathway for carotenoid biosynthesis.

Amitrole acts at the third site for herbicides that inhibit carotenoid biosynthesis—cyclisation. Lycopene, a linear intermediate, is cyclised (6-atom rings) at both ends to form the carotenes, which can in turn be hydroxylated to form the xanthophyll carotenoids. Amitrole inhibits cyclisation of lycopene.

Amitrole may also affect cell division and elongation.

For more information, see Plant & Soil Sciences eLibrary: Herbicides that act through photosynthesis. Inhibitors of carotenoid biosynthesis.

2Q.2 Absorption into the plant

Amitrole is highly water-soluble and is absorbed by the roots (Table 2). It also rapidly penetrates the leaf cuticle. Root uptake tends to be minor because amitrole is quickly decomposed in the soil. Amitrole may be partially bound to cuticular waxes depending on the species. Diffusion across the plasma membrane is likely to be a passive process.

Clomazone is poorly absorbed through the cuticle and epidermis and poorly translocated in the phloem. However, it is readily absorbed by roots and emerging shoots (i.e. the coleoptile of grasses and the broadleaf hypocotyl).

Table 2: *Environmental characteristics of Group Q herbicides.*

Group Q class	**Active ingredient**	**Example trade name**	**Water solubility (mg/L)**	**Log *K*ow**	**Soil persistence (half-life @ 20°C) (field)**	**Soil mobility (*K*oc/*K*foc)**	**Volatility (Henry's Law constant, 25°C)**
Isoxazolidinones	Clomazone	Magister®	1102	2.54	43	300, moderate	Moderately volatile
Triazoles	Amitrole	Alliance®	264,000	–0.97	16	87, moderate	Non-volatile

Log Kow, ratio of herbicide that is soluble in octanol (organic solvent) v. water; it is a good indicator of the lipophilic or hydrophilic nature of a herbicide; the larger the log Kow value the more lipophilic the herbicide; herbicides with values between –1 and 1 should move in the phloem following foliar application. Koc/Kfoc: >1000, binds strongly to soil; <500, moves in water.

Source: Pesticides Properties Database, http://sitem.herts.ac.uk/aeru/ppdb/en/index.htm

2Q.3 Translocation within the plant

Amitrole is polar and non-ionised and is strongly mobile in both the phloem and xylem. It is largely retained in the phloem once it has crossed the plasma membrane. The herbicide accumulates at the growing points.

Clomazone is translocated in the xylem to the growing points.

2Q.4 Symptoms

Symptoms on larger plants begin with bleaching of the new growth. This bleaching and yellowing spreads through the plant and leads to wilting and necrosis or browning.

Seedlings will emerge from clomazone-treated soil, but are bleached and become necrotic after several days.

Larger plants treated post-emergent with clomazone show bleaching of the leaves. Similar symptoms occur in adjacent plants with vapour drift from post-emergent applications.

2Q.4.1 Timeframe for symptoms and plant death

Rate of development of symptoms and subsequent damage and death depend on the plant species, herbicide dose, age and size of plant, and rate of plant growth. After application, death occurs from as early as several days for emerging seedlings to four to eight weeks for larger plants.

Compared with glyphosate, the development of symptoms and the death of weeds treated with amitrole are very slow.

Photo 1: *Amitrole causing bleaching on new growth in barley.*

Photo: Andrew Storrie, Agronomo

Photo 2: *Amitrole causing bleaching in canola.*

Photo: Andrew Storrie, Agronomo

2Q.5 Crop selectivity

Amitrole is non-selective (Table 3). It does exhibit some synergism when mixed with paraquat (Group L). Amitrole decomposes quickly in the soil, so it is unlikely that there will be root uptake.

When using clomazone, the main tactic for crop selectivity is separation from the band of chemical. This is similar to the requirement with Group D herbicides. Clomazone should not be applied to soil intended for seedling transplants (except for tobacco).

Rice can detoxify clomazone quickly, unless it receives direct herbicide contact or it is stressed from cold, deep water or salinity.

Table 3: *Differences in efficacy between Group Q chemical classes.*

Group Q class	Herbicide example	Crops	Weeds
Isoxazolidinones	Clomazone	Rice	*Echinochloa* spp., suppresses silvertop grass (*Leptochloa fusca*)
		Cucurbits, green beans, navy beans, poppies, potatoes, tobacco	Post-plant pre-emergent and post-emergent control of a range of broadleaf weeds
Triazoles	Amitrole	Orchards, vineyards, eucalyptus and pine plantations, canola, wheat, barley, oats, rye, triticale, faba beans, field peas, lupins, cotton, mung beans, sorghum, potatoes, a range of pastures	Wide range of grasses, non-grass monocots and broadleaf species

2Q.6 Effect of environmental conditions on activity

Clomazone is poorly translocated from a foliar application. Absorption via the roots is important for effective control; therefore, available soil moisture is one of the critical factors in determining the efficacy of this herbicide.

Clomazone should not be used on soils that contain <15% clay and 2% organic matter. (This does not apply to tobacco or poppy crops, which have a higher tolerance to clomazone at label rates.)

MORE INFORMATION

See the comprehensive GRDC Spray Application GrowNote for more information.
https://grdc.com.au/Resources/GrowNotes-technical/Spray-Application-Manual

2Q.6.1 Light

Group Q herbicides need light to produce damaging radicals within the photosynthetic system. Bright sunlight will speed development of symptoms and ultimately will speed control.

2Q.6.2 Temperature

As temperature increases, the rate of photosynthesis increases, speeding the production of radicals within the photosynthetic system. Frosts and cold stress will reduce the effectiveness of these herbicides.

2Q.6.3 Humidity

Plants growing in higher humidity have less epidermal wax on the leaf surface than plants growing in low humidity. High humidity (>50%) will increase the amount of amitrole entering the plant, owing to a hydrated cuticle and the likelihood of thinner cuticular waxes. High humidity will increase the life of herbicide droplets on the leaf, increasing the time for diffusion to occur.

2Q.6.4 Soil moisture stress

Moisture-stressed plants have thicker cuticles, and these will slow the absorption of foliar-applied amitrole. Addition of certain adjuvants can assist herbicide absorption into the plant.

Adequate moisture is required at the soil surface to enable root absorption of clomazone. Drying of the surface soil will reduce the level of weed control when using this herbicide.

Clomazone use in rice is not affected by moisture stress because it is applied at permanent flood.

2Q.6.5 Rainfall

The rain-fast period for foliar application of amitrole is six hours.

Light rain will improve plant uptake of clomazone from the soil.

2Q.7 Spray application

Amitrole is well translocated within the plant; however, it is not as active a herbicide as glyphosate, so it requires good coverage to maximise the amount of herbicide entering the plant.

Product labels (e.g. Amitrole T) recommend applying 100–500 litres (L) per hectare for optimum coverage, but they do not mention spray quality. Medium to coarse spray quality should be used, depending on the situation.

If amitrole is in a tank mix with paraquat, application must be as a medium to coarse (Alliance®) or medium (Para-Trooper) spray quality. Target coverage should be 10–15% as measured with water-sensitive paper.

Soil-applied herbicides need even coverage; however, they can be applied in a coarse to extremely coarse spray quality. The clomazone label recommends at least a medium spray quality, although this is more aimed at drift reduction. If tank-mixed with a knockdown herbicide, application should be in the relevant spray quality for that knockdown herbicide.

MORE INFORMATION

See the comprehensive GRDC Spray Application GrowNote for more information.
https://grdc.com.au/Resources/GrowNotes-technical/Spray-Application-Manual

See the GRDC Adjuvants Booklet
https://grdc.com.au/resources-and-publications/all-publications/publications/2015/04/adjuvants-booklet

2Q.7.1 Adjuvants

Amitrole and amitrole + paraquat mix may need addition of a non-ionic surfactant if application volumes are below 400 mL per 100 L solution.

If clomazone is applied by air, it must have a drift retardant added.

2Q.7.2 Water quality

Amitrole is not affected by a wide range of water qualities. However, when tank-mixed with paraquat the water requirements for paraquat must be adhered to, i.e. water should be clean and free from clay, silt and algae.

Hard water should be avoided when using clomazone.

2Q.8 Further reading

Caseley JC (1987) Effects of weather on herbicide activity. In 'Eighth Australian Weeds Conference'. pp. 386–394.

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Herbicide Group Z modes of action

The Group Z Mode of Action (MoA) herbicides have unknown and diverse sites of action. This makes Group Z the receptacle for herbicides that do not fit into other groups. This is partly because we are still unclear about how these herbicides work despite their use for decades.

Group Z are also classified as Group Z by the global Herbicide Resistance Action Committee (HRAC). Because each class of chemical acts on different pathways, the Weed Science Society of America (WSSA) classifies flamprop-m-methyl as Group 25 and organoarsenicals as Group 17, whereas endothal is not classified (NC) (http://hrac.tsstaging.com/tools/classification-lookup).

Flamprop-m-methyl is used for the post-emergent control of wild oats in bread wheat and triticale.

In Australia, endothal is registered for the control of winter grass in turf. In the northern hemisphere, it has been used as a post-plant incorporated herbicide in sugar beets to control annual broadleaf and grass weeds, and as a pre-harvest desiccant in potatoes and alfalfa (lucerne) and clover seed crops. It has also been used as an aquatic herbicide to control algae and a number of submerged aquatic weeds.

Different forms of arsenic have been used as herbicides since the early 1900s. The organoarsenical herbicide MSMA (monosodium methyl arsenate) is used for post-emergent control of annual and perennial grasses and broadleaf weeds in cotton, sugarcane and non-crop areas, control of *Opuntia* spp., control of annual grasses in turf, and control of burrs in cotton and non-crop areas. The organoarsenical herbicide DSMA (disodium methyl arsenate) is used for post-emergent control of annual grasses in turf. Use of organoarsenical herbicides has declined markedly during the past 15 years.

There are three chemical classes within the Group Z MoA as shown in Table 1.

Table 1: *Herbicides included in Group Z.*

Chemical class	Active ingredient	Product examples
Arylaminopropionic acids	Flamprop-m-methyl	Judgement®
Dicarboxylic acids	Endothal	Poachek®
Organoarsenicals	DSMA	Trinoc
	MSMA	Daconate®

Trinoc contains more than one active constituent.

Source: http://www.croplife.org.au/resistance-strategy/herbicide-mode-of-action-groups/

2Z.1 Mode of action and biochemical pathways

Flamprop-m-methyl is a mitotic disrupter with an anti-microtubule mechanism of action that affects orientation of spindle and phragmoplast microtubules, possibly by minus-end microtubule disassembly.

Endothal inhibits lipid and protein synthesis in some species while causing increased electrolyte leakage and increased levels of polyphenols, followed by necrosis.

MSMA and DSMA are thought to affect cell membrane integrity.

2Z.2 Absorption into the plant

Flamprop-m-methyl is a pre-herbicide and is converted to the active form inside the plant. It is readily absorbed through the cuticle and epidermis of the plant.

Endothal is rapidly absorbed by roots and can rapidly penetrate the leaf cuticle as the undissociated parent acid.

Organoarsenicals are readily absorbed by foliage.

2Z.3 Translocation within the plant

Flamprop-m-methyl appears to be well translocated within the phloem.

Endothal is translocated from the roots to foliar parts of the plant by the xylem; it is not phloem-mobile. Endothal can cause callus formation in the phloem sieve tubes, which helps to limit phloem mobility.

Organoarsenicals are translocated in both the phloem and xylem because they are weak acid herbicides with high levels of water solubility (Table 2).

Table 2: *Environmental characteristics of Group Z herbicides.*

Group Z class	Active ingredient	Example trade name	Water solubility (mg/L)	Log *K*ow	Soil persistence (half-life @ 20°C) (days)	Soil mobility (*K*oc/*K*foc)	Drift potential (Henry's Law constant, 25°C)
Arylaminopropionic acids	Flamprop-m-methyl	Judgement®	35	3.33	10	n.a.	Non-volatile
Dicarboxylic acids	Endothal	Poachek®	100,000	1.91	7	85, moderate	Non-volatile
Organoarsenicals	DSMA	Trinoc	43,200	–5.3	269	1680, slight	Non-volatile
	MSMA	Daconate®	580,000	–3.1	200	n.a.	Non-volatile

Log Kow, ratio of herbicide that is soluble in octanol (organic solvent) v. water; it is a good indicator of the lipophilic or hydrophilic nature of a herbicide; the larger the log Kow value the more lipophilic the herbicide; herbicides with values between –1 and 1 should move in the phloem following foliar application. Koc/Kfoc: >1000, binds strongly to soil; <500, moves in water. n.a., Not available.

Source: Pesticides Properties Database, http://sitem.herts.ac.uk/aeru/ppdb/en/index.htm

2Z.4 Symptoms

Application of flamprop-m-methyl leads to rapid cessation of growth and a change in the plant colour to a blue-green. The youngest leaf unrolls and tiller sheaths begin to open and detach from the shoot. High rates of herbicide lead to plant death, whereas spray-topping rates and timing lead to the inflorescence not fully emerging from the boot. The inflorescence appears as though it has been stem-frosted.

Endothal causes rapid desiccation and browning of foliage. Endothal present in the soil and absorbed by the roots causes shortening of roots.

Organoarsenicals causes chlorosis with little or no wilting, leading to desiccation. Cotton seedlings can exhibit reddening.

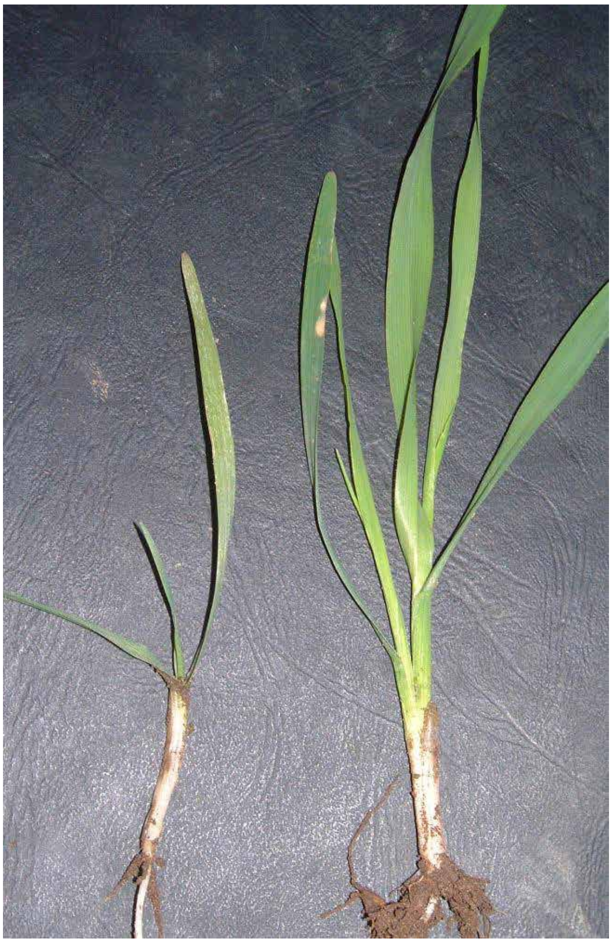

Photo 1: *Oat on the left sprayed with Judgement® (flamprop).*

Photo: Harm van Rees

2Z.4.1 Timeframe for symptoms and plant death

Rate of development of symptoms and subsequent damage and death depend on the plant species, herbicide dose, age and size of plant, and rate of plant growth.

Flamprop-m-methyl will cause subtle changes within two to three days after application. Plant growth ceases within hours. Plant discoloration and death can take one to five weeks.

Organoarsenicals will cause severe chlorosis and desiccation in less than one day with high temperatures and light. Symptoms may take five to 10 days to appear at temperatures <25°C.

2Z.5 Crop selectivity

Selectivity of flamprop-m-methyl depends on the methyl ester undergoing hydrolysis to form the biologically active acid, which is usually detoxified quickly in wheat and triticale by conjugation (Table 3). Cultivars containing the *SR26* stem rust gene are known to be more susceptible to this herbicide than other cultivars.

Photo 2: *Judgement® (flamprop) damage to a wheat leaf.*

Photo: David Pfeiffer

Selectivity with endothal appears to be rapid metabolism within the plant.

The organoarsenicals herbicides are conjugated with sugars, amino acids, other organic acids and other molecules to make them nontoxic.

Table 3: *Differences in efficacy between Group Z chemical classes.*

	Herbicide	Crops	Weeds
Arylaminopropionic acids	Flamprop-m-methyl	Bread wheat and triticale	Post-emergent control of wild oats (*Avena* spp.)
Dicarboxylic acids	Endothal	Turf	Post-emergent control of winter grass (*Poa annua*)
Organoarsenicals	DSMA	Turf	Post-emergent control of annual grasses
	MSMA	Cotton, sugarcane, non-crop areas, couch turf	Post-emergent control of a range of grass and broadleaf species, *Opuntia* spp.

2Z.6 Effect of environmental conditions on activity

2Z.6.1 Light

Photodegradation is not a major path of breakdown. High levels of light increase the speed of action of organoarsenical herbicides.

2Z.6.2 Temperature

Warmer temperatures speed the action of flamprop-m-methyl and organoarsenicals, with temperatures >20°C recommended for application. Increased plant growth rates increase the translocation of these herbicides, speeding the effect in susceptible species and increasing the rate of herbicide metabolism in tolerant species.

Endothal should not be used when temperatures exceed 25°C because it will scorch the turf.

2Z.6.3 Humidity

Low relative humidity increases the speed of development of symptoms with organoarsenicals.

2Z.6.4 Soil moisture

Adequate soil moisture is required to maintain active plant growth to assist with translocation of the herbicides and blocking of the targeted chemical pathway.

Flamprop-m-methyl is particularly sensitive to moisture stress because it is mainly translocated in the phloem.

2Z.6.5 Rainfall

MSMA has a six-hour rain-fast period, and the label for Trinoc (DSMA + MCPA) states four hours. Flamprop-m-methyl is rain-fast after four hours. Differences are due to differential rates of absorption into the leaf.

2Z.7 Spray application

Flamprop-m-methyl should be applied as a medium spray-quality droplet in up to 100 litres spray volume.

The label for Poachek® (endothal) suggests that it should be applied with a fine spray. This is contrary to good practice, and endothal should be applied as a medium spray quality with an application volume to give high levels of coverage, such as 100–200 litres per hectare.

Labels for MSMA and DSMA do not recommend a spray quality, but they should be applied as a coarse spray quality with a sufficiently high application volume to give at least 15% coverage. Off-target movement of organoarsenicals herbicides should be avoided.

MORE INFORMATION

See the comprehensive GRDC Spray Application GrowNote for more information. https://grdc.com.au/Resources/GrowNotes-technical/Spray-Application-Manual

See the GRDC Adjuvants Booklet https://grdc.com.au/resources-and-publications/all-publications/publications/2015/04/adjuvants-booklet

2Z.7.1 Adjuvants

A crop oil should be added to flamprop-m-methyl only for spray-topping.

Endothal does not require an adjuvant.

Organoarsenicals do not need adjuvants; they are weak acids and highly water-soluble.

2Z.7.2 Water quality

Organoarsenicals are sensitive to hard water because they are weak acids. High levels of cations, including iron, lead to the formation of insoluble forms, which precipitate in the tank.

Flamprop-m-methyl and endothal are not sensitive to water quality.

2Z.8 Further reading

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