# SOIL BEHAVIOUR OF PRE-EMERGENT HERBICIDES IN AUSTRALIAN FARMING SYSTEMS

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# INTRODUCTION

## The importance of controlling weeds in broadacre field crops

Weed management is critical for profitable Australian farming systems. Weeds compete aggressively with grain crops for moisture and nutrients and if left unchecked, can result in significant crop losses.

In addition to losses from competition, Australian growers spend well over $1 billion[1] per year on herbicides to which the additional costs of machinery, labour and contractors to apply these herbicides must be added.

The past 30 years has seen a major revolution in broadacre farming with the majority of grain farmers adopting a minimum or zero tillage system which has largely reduced or removed the use of cultivation as a tool for weed control. Also, in many areas, there has been a trend towards growers specialising in 'cropping'. This has led to a decline or elimination of livestock from the farming system, further reducing the diversity of weed control options on many properties. The combined effect has been a significant increase in the reliance on herbicides for weed management in Australian farming systems.

This shift in farming system has seen an evolutionary change in weed species in many paddocks, with increasing dominance of surface or shallow germinating weeds that are suited to a zero tillage system where weed seeds are predominantly left undisturbed on the soil surface.

Since the adoption of reduced tillage practices, controlling weeds on the modern farm has largely become the domain of herbicides, both within the crop and in the fallow between crops. Growers have had a range of cost effective and efficacious herbicides to rely upon, however there has been a heavy reliance on a few individual modes of action, namely Groups A, B, I and M in particular.

While being quite different in their weed control spectrum and the way that they work within the plant, these herbicide groups have a number of similarities that have seen them gain popularity:

- They provide reliable, consistent performance
- Are frequently 'cheap' relative to other available weed control options, and
- They work primarily as foliar applied post-emergence herbicides.

The cost effectiveness, reliability and ease of use of these herbicides, has encouraged growers to favour post emergent options, where they can wait and see which weeds emerge before dealing with the problem.

Unfortunately, evolution continues to work in our cropping systems. This has seen an increase in the importance of weeds that:

a) Are adapted to the new farming system i.e. surface germinating and windblown weed seeds and

b) Selection of individual weeds that are resistant to the herbicides previously used to control them.

A recent example of adaptation and evolution is evident in barley grass and brome grass. Continual herbicide selection pressure early in the cropping season has selected for individuals that express a high level of seed bank dormancy leading to a high percent of the population emerging later in the season and escaping early season control. This is driven by the selection of a vernalisation response (cold requirement before germination) which is under the control of a single gene.

Herbicide resistance and species shift are causing many advisers and growers to radically rethink their approach to weed management including the introduction of more diversity into their weed control programs. Increased use of pre-emergent herbicides is one tool that increases diversity of the weed control program while also reducing weed numbers, which complements the use of tactics such as crop competition, in-crop herbicides and harvest weed seed control. However increased use of pre-emergent herbicides will also increase the selection pressure placed on these herbicides; underscoring the need to introduce non-herbicide based weed management tactics into the cropping system, to reduce our reliance on herbicides and thereby prolonging their useful life.

## The value of pre-emergent herbicides

When devising a weed control strategy, pre-emergent herbicides can be a valuable additional tactic to help drive weed numbers down. Used alone, they often do not achieve the objective of driving down weed seed bank numbers as small numbers of weed escapes often occur and provide seed bank replenishment. However, when used as a component amongst a suite of tactics, they can be particularly effective.

Benefits of pre-emergent herbicides include:

- Offers an alternate mode of action to many post-emergent options
- Reduced selection pressure on subsequent post-emergent herbicide applications

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[1] Manufacture level sales of $1.26m for 2012/13 as reported in the Commonwealth of Australia Gazette No. APVMA 4, Tuesday 25 February 2014, Page 29

- Removal of early season weed competitive pressure often protects crop yield better than later applied post-emergent applications, especially in weedy paddocks
- Cost savings, especially in the fallow where multiple knockdown applications may be required
- Reduced time pressure on other spraying operations, both in crop and in fallow
- Major role in patch eradication where a weed blow-out can be GPS logged and a pre-emergent herbicide applied to manage the patch
- After a cultivation event, there will always be some weed seed in a position in the soil profile that is ideal for germination. Applying a pre-emergent herbicide after the last cultivation can manage these weeds that would otherwise emerge and ultimately return additional seed to the soil, and
- Some crops have few post-emergent options (e.g. grass weed control in sorghum, or broadleaf weed control in pulses) and hence often rely on pre-emergent herbicides for in-crop weed control.

## Common objections to the use of pre-emergent herbicides

Many growers frequently raise objections when pre-emergent herbicides are discussed. Some of the more common objections are:

***"If it doesn't rain to germinate the weeds then my money is wasted".***

Most pre-emergent herbicides require rain for incorporation and uptake, although some pre-emergent herbicides can remain on a dry surface for considerable time without degradation. Understanding the properties of the chosen herbicide assists decision making on application timing and the incorporation requirements of the molecule. Usually rainfall, or existing soil moisture, is required to germinate weeds, so the correct timing of pre-emergent herbicide application relative to rainfall and weed germination is important to maximise the value of the investment.

***"I applied a pre-emergent herbicide a few years ago and it didn't work. I can't rely on them".***

Pre-emergent herbicides are not all the same. The properties of each herbicide dictate where it remains in the soil profile, what conditions are required to maximise performance and how quickly it will break down. As pre-emergent herbicides are strongly influenced by soil type, stubble cover, incorporation, temperature and rainfall, it is quite possible that a different result can be achieved between two adjacent paddocks with application only a few weeks apart.

It is generally much easier to monitor the performance of a post emergent herbicide. The starting weed population is known and the herbicide effects can be seen over the resulting weeks. With commercial pre-emergent herbicide applications, usually the whole paddock is treated so the magnitude of the weed pressure may be underestimated. As a result, it is usually much more difficult to gauge success and impact of a pre-emergent herbicide application, than it is for a post-emergent application. In situations where growers have been dissatisfied with the performance of a pre-emergent herbicide, they are often surprised if a 'missed strip' is found, as this demonstrates what the paddock would be like if the pre-emergent herbicide had not been used.

***"Pre-emergent herbicides leach and move in the soil and damage off target vegetation".***

The properties of some pre-emergent herbicides allow the product to be more available in the soil profile and more able to move with the soil water; while some other herbicides are very tightly bound and unlikely to move. Understanding herbicide properties, in particular the solubility and binding, enables the right product to be selected for the situation.

***"Using pre-emergent herbicides locks me out of crop rotation options".***

This is probably the most frequent objection by growers when their adviser recommends a pre-emergent herbicide. By nature of their residual properties, most pre-emergent herbicides will have plantback constraints to some crops.

However, it is extremely unlikely that a grower will ever apply a particular residual herbicide to the entire farm, so the 'whole farm' is not being locked out of a flexible crop rotation. In practice, there is usually a percentage of paddocks where the next crop rotation is firmly locked in. In these paddocks, there is the option to select an appropriate residual herbicide with only a low risk of a negative impact on crop rotations.

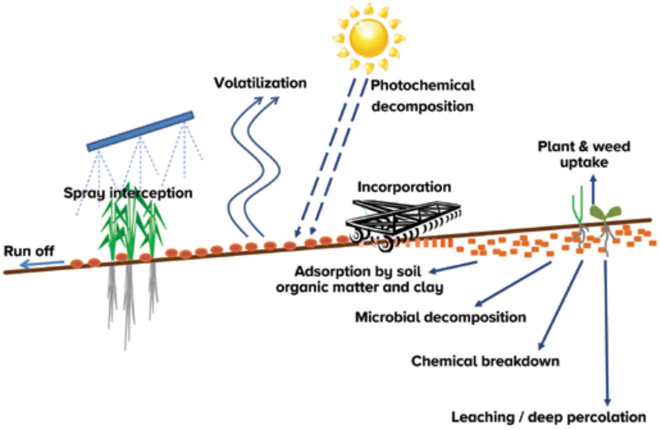
When dealing with these common objections, the key underlying theme is that it is critical for advisers to have a thorough understanding of the properties of pre-emergent herbicides under consideration, to enable the best choice to be made.

This manual is a reference for Australian grain advisers, covering the factors influencing the performance and break down of pre-emergent herbicides.

# FACTORS INFLUENCING THE ACTIVITY OF PRE-EMERGENT HERBICIDES

To understand how pre-emergent herbicides perform, it is important to know the properties of the herbicide, the soil type and how it is broken down in the environment. Availability of a pre-emergent herbicide is an interaction between the solubility of the herbicide; how tightly it is bound onto soil colloids and organic matter; soil factors such as structure, cation exchange capacity and pH; herbicide volatility; the environment and particularly soil water and the rate of herbicide applied.

**Figure 1:** Interactions, loss and breakdown pathways of soil applied herbicides.



Understanding the importance of each of these pathways will give guidance as to likely performance of the herbicide in question. However, if one of these factors in the equation is extreme, then this single factor can have an overriding influence on the overall balance and can alter what normally happens in the field.

For example, some herbicides are relatively insoluble and tightly bound to soil colloids which suggest that they are unlikely to leach. However, in a situation of a high initial rainfall event occurring onto a dry soil, even a herbicide with these properties may be moved further down the soil profile before it has the opportunity to bind to the soil. This may mean that the herbicide can move out of the zone where it is required for weed control, or into a zone where it can damage the crop.

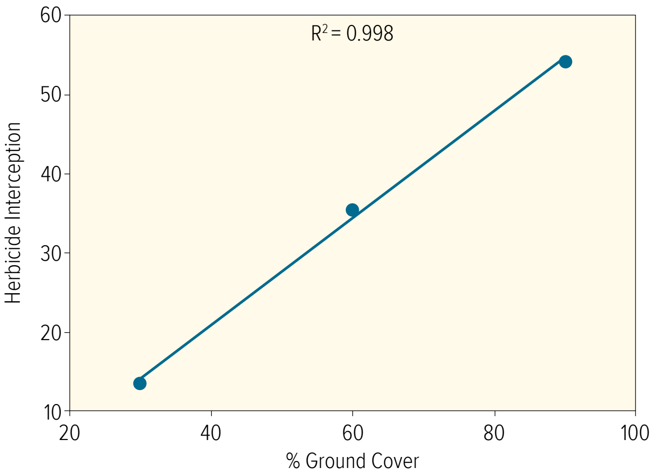
## Interactions prior to incorporation

### Stubble and crop interception

Stubble or existing weed cover in a zero or reduced till fallow will intercept some pre-emergent herbicide before it reaches its target – the soil. Likewise, if the pre-emergent herbicide is applied as an in-crop application, a percentage of herbicide will be intercepted by the crop.

The amount of herbicide intercepted will be proportionate to the percent of ground coverage of the stubble or crop (or weeds if they are already present at application). As shown in Figure 2, while this relationship is linear it should be noted that, for example, 50% ground cover does not result in 50% capture of the herbicide on the above ground material.

**Figure 2:** The percentage of herbicide captured by stubble or plant material in relation to the percentage of ground cover Shaner D. (2013).



Interception by standing material can have two negative effects:

a) For some products, herbicide tied up on the stubble or in the canopy may not be available for soil incorporation and subsequent weed control, and

b) Interception may lead to an uneven coverage of the soil surface, resulting in areas with insufficient herbicide coverage and potentially weed escapes.

Herbicide intercepted by standing organic material will be subject to a certain level of binding, depending on the herbicides' characteristics (see later section on binding). Some herbicides are tightly bound to crop residues and become lost to the system in terms of weed control, despite subsequent rainfall (for example trifluralin). Others are loosely bound and relatively soluble and can be returned to the soil by rainfall that 'washes' herbicide off the organic material (for example chlorsulfuron). To understand the potential level of binding of a herbicide, advisers need to consider its binding coefficient ($K_d$ or $K_{oc}$) and solubility (see page 11-12). However, even if a herbicide is loosely bound and available to be washed off, it still may be prone to loss due to volatility and photodegradation, before it is incorporated into the soil by rainfall.

Where high levels of stubble or plant material exist, the level of spray droplet interception can be minimised by adjusting how the herbicide is applied. Some techniques that can increase the proportion of herbicide reaching the soil include:

- Wind across the rows during application
- Use rear facing nozzles where the angle offsets the travel speed, to have droplets moving predominantly downwards through the stubble
- Larger droplets travelling at higher speed
    - Select a nozzle and pressure that produces larger droplets
    - Narrow fan angles (e.g. 65-80 degrees) increases droplet speed
- Keep water rates high to maintain coverage when using larger droplets by increasing the number of droplets produced.
- Narrower nozzle spacing (25cm vs 50cm)
- Slower travel speeds (i.e. < 16 km/h) to reduce horizontal movement (forward trajectory of droplets), and
- Minimise boom height, but ensure at least double overlap.

**For more information on maximising application with pre-emergent herbicides**

**https://www.youtube.com/embed/s63GYYyflzw?start=200&end=473**

In situations where pre-emergent herbicides are used in-crop, correctly set up directed sprays (layby application) are designed to reduce interception by directing the spray under / away from the crop canopy.

Where herbicides with both pre and post-emergent activity are applied in-crop, the pre-emergent activity is often better when applied during early crop growth stages, as soil coverage may be more even. This is due to less crop interception prior to droplets meeting their target – the soil surface.

## Pre-emergent herbicides and windrow burning

With the advent of increasing herbicide resistance, many growers have introduced windrow burning into their integrated weed management strategy. This technique concentrates the previous year's stubble, including the chaff fraction containing the weed seeds, into a narrow band to be burnt in autumn.

If pre-emergent herbicides are used in conjunction with this technique, then consider the following points:

- Applying pre-emergent herbicides over the top of a windrow before it is burnt, will probably result in extremely high levels of herbicide interception and very little on the soil surface under the windrow. So avoid herbicide application prior to burning.
- Always strive for a hot burn within the windrow. This is important to obtain maximum mortality of the weed seeds, but also to maximise the amount of residue converted to ash and minimise the amount left as charcoal. Any unburnt chaff (which will contain high concentrations of weed seeds) can reduce pre-emergent herbicides reaching the soil.

Windrow burning at Pithara WA.
Photo: Evan Collis Photography

- Herbicides will not generally bind tightly when sprayed onto ash. However, a thick layer of ash may prevent even soil coverage, unless a rainfall event has occurred between the burning and the herbicide application, to disperse the ash.
- Conversely, herbicides will usually bind to charcoal to an even greater extent than they do for green organic matter or stubble. Where charcoal is left after a burning event (or biochar is added to the soil) then it is likely that less herbicide will be available for weed control and herbicide performance may be compromised.

## Photodegradation

Photodegradation occurs when the herbicide undergoes a chemical reaction in the presence of sunlight and is then broken down and lost to the weed control system. For most uses of pre-emergent herbicides in Australia, photodegradation is not a significant path of breakdown as standard incorporation practices such as cultivation, sowing or sufficient rainfall after application are typically adequate to prevent unacceptable levels of loss. However, when a herbicide is sprayed onto a dry soil surface or dry stubble in summer, with no following rainfall or mechanical incorporation, losses from this pathway will be at their highest.

Some of the common pre-emergent herbicides that can undergo some level of photodegradation include the Group C herbicides (atrazine, fluometuron, simazine, terbuthylazine and diuron); the Group B herbicide sulfosulfuron; the DNA herbicides pendimethalin and trifluralin; the PPO inhibitors oxyfluorfen and saflufenacil and the Group K herbicide s-metolachlor.

**Table 1: Potential loss from photodegradation of selected residual herbicides used in Australian broadacre cropping.** *Shaner, D. (2014).*

| | | | |
|---|---|---|---|
| B | | sulfosulfuron | Half-life 3 days |
| C | **triazines** | atrazine | Half-life 45 days on a sandy loam @ 25°C and pH 7.5 |
| | | prometryn | Negligible loss after 30 days on sandy loam @ 15-28°C |
| | | simazine | Half-life 21 days on a sandy loam at 25°C |
| | | terbuthylazine | Half-life < 40 days |
| | **ureas** | diuron | Not strongly photodegraded, but losses can be significant if diuron remains on the soil surface for several days or weeks. |
| | | fluometuron | Half-life 9.7 days on a sandy loam @ 10-36°C |
| | **triazinones** | metribuzin | Insignificant (0.05-0.28% per day) |
| D | **dinitroanilines (DNA's)** | pendimethalin | <5% loss after 30 days from a sandy loam held at 10.2% moisture |
| | | trifluralin | Half-life 44 days. |
| G | **diphenylethers** | oxyfluorfen | Half-life 20-30 days on dry soil |
| | **pyrimidindiones** | saflufenacil | Half-life of 66 days under soil photolysis |
| K | | s-metolachlor | Half-life 8 days on sandy loam @ 15-52°C |

Note: After incorporation has occurred, further losses from photodegradation will be minimal. After incorporation, other degradation pathways will be the primary determination of herbicide loss.

If these herbicides are applied under warm, dry conditions with no rainfall or mechanical incorporation in the coming weeks, losses can be significant.

## Volatilisation

Some pre-emergent herbicides used in the Australian grains industry are considered volatile. Volatile herbicides transition to a gaseous phase after application if left on the soil surface without incorporation. Some higher volatility herbicides should be incorporated soon after application to avoid significant loss to the atmosphere and therefore maintain their efficacy on weeds.

**For more information on volatilisation and incorporation by sowing**

**https://www.youtube.com/embed/LJNjuMWS57U?start=231&end=516**

Loss from volatility is not an 'on/off' switch. For example, if a herbicide label indicates that the product should be "incorporated within 24 hours" this does not mean that there is no loss up until hour 23 and that it is all gone by the 25th hour. Volatility loss commences as soon as the spray has dried, so with any volatile herbicide it is important to incorporate as soon as possible after application. The time period for incorporation on a label is the time by which the manufacturer has determined that losses may start to become unacceptably high if the product has not been incorporated within this time.

Volatility is measured as vapour pressure and is usually expressed as millipascals (mPa) at 20 to 25°C Herbicides with a low vapour pressure (i.e. less than 1 mPa) are generally referred to as 'non-volatile', while products with a vapour pressure above 1 mPa may convert into a gaseous phase and be lost to the atmosphere, unless incorporated post application. As the vapour pressure increases, so does the urgency to have the herbicide incorporated quickly, to reduce losses.

Table 2 lists some common pre-emergent herbicides in order of volatility to demonstrate the range of vapour pressures.

**Table 2: Examples of vapour pressure for selected pre-emergent herbicides and summary of incorporation requirements.**

| Active ingredient (Herbicide) | Vapour Pressure (mPa @ 20 to 25°C)^ | |
|---|---|---|
| tri-allate (Avadex®) | 12 | Active ingredients with a vapour pressure of greater than 1 mPa are generally considered volatile and are likely to require or benefit from incorporation. Refer to individual product labels for specific situations. |
| trifluralin (Treflan®) | 9.5 | |
| s-metolachlor (Dual®) | 3.7 | |
| pendimethalin (Stomp®) | 3.34 | |
| dimethenamid-P (Outlook®) | 2.5 | |
| clopyralid (Lontrel®) | 1.36 | |
| prosulfocarb (Arcade®) | 0.79 | Active ingredients with a vapour pressure of less than 1 mPa are generally considered low or non-volatile and do not usually require any specific incorporation recommendations after application. |
| flumioxazin (Terrain®) | 0.32 | |
| terbuthylazine (Terbyne®) | 0.152 | |
| metribuzin (Sencor®) | 0.121 | |
| metazachlor (Butisan®) | 0.093 | |
| propyzamide (Rustler®) | 0.058 | |
| imazapic (Flame®) | 0.01 | |
| atrazine (Gesaprim®) | 0.0039 | |
| triasulfuron (Logran®) | 0.0021 | |
| simazine (Gesatop®) | 0.00081 | |
| isoxaflutole (Balance®) | 1.0 x 10-3 | |
| diuron (various) | 1.15 x 10-3 | |
| pyroxasulfone (Sakura®) | 2.4 x 10-3 | |
| diflufenican (Brodal®) | 4.25 x 10-3 | |
| picloram (Tordon®) | 8.0 x 10-5 | |
| chlorsulfuron (various) | 3.07 x 10-6 | |

^ University of Hertfordshire. (2006-2019). The Pesticide Properties DataBase (PPDB) developed by the Agriculture & Environment Research Unit (AERU), University of Hertfordshire. Accessed on 2nd October 2019 http://sitem.herts.ac.uk/aeru/iupac/index.htm

## How quickly is trifluralin lost without incorporation?

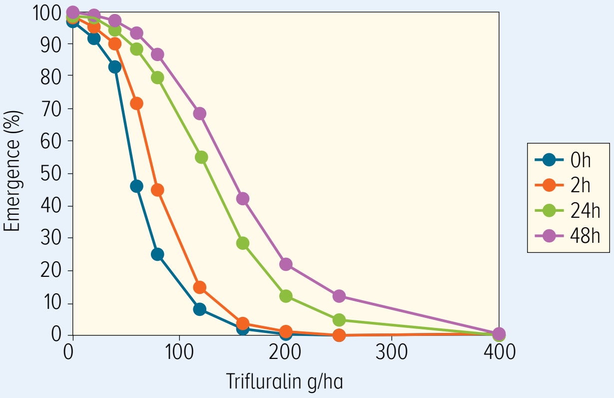
The speed of herbicide loss to volatility depends on many factors, many of which are specific to each application. Factors that affect volatility loss include:

- air temperature (higher temperatures increase the speed of volatilisation)
- moisture (volatility generally increases with higher moisture)
- the type of substrate (e.g. soil surface, stubble)
- soil type (volatility will generally be higher on soils with less binding potential)
- wind speed (volatility will generally increase with increasing air flow across the treated surface
- the volatility of the compound.

The vapour pressure of a herbicide can be measured under a controlled set of conditions and provides one measure to compare herbicides i.e. the higher the vapour pressure the faster the herbicide will be lost, all other things being equal. The vapor pressure of trifluralin is reported as 9.5 mPa @ 20°C, making it potentially one of the more volatile pre-emergent herbicides used in broadacre grain production.

An interesting trial conducted under controlled temperatures sought to evaluate the impact of volatility loss on trifluralin on annual ryegrass when incorporation was delayed by up to 48 hours. Pots of sandy, alkaline soil had trifluralin applied at a range of application rates, with incorporation at 0 (incorporated immediately), 2, 24 and 48 hours after application. Annual ryegrass was planted after the last incorporation timing. The pots were then kept indoors to minimise loss from UV light and wind. Herbicide dose response curves were generated.

**Figure 3:** Effect of time until incorporation and trifluralin application rate on mean emergence of annual ryegrass (of 25 seeds sown), in an alkaline, sandy soil. Eureka! AgResearch. (2015).



As can be seen from Figure 3, delaying incorporation significantly increased the amount of trifluralin required to obtain the same level of control.

ED$_{50}$ values (estimated dose to achieve 50% control) were established and a percentage loss due to trifluralin volatility was calculated.

**Table 3: ED$_{50}$ and trifluralin loss with time to incorporation on an alkaline, sandy soil.** Eureka! AgResearch. (2015).

| Incorporation time after herbicide application (hours) | 0 hrs | 2 hrs | 24 hrs | 48 hrs |
|---|---|---|---|---|
| ED$_{50}$ (gai/ha) | 57 | 75 | 136 | 150 |
| Est. % trifluralin lost | 0% | 24% | 58% | 62% |

## Incorporation

Without incorporation, some herbicides are more predisposed to breakdown and loss from volatilisation and/or photodegradation. Some active ingredients are quite volatile and significant losses from the soil surface can occur if the herbicide is not incorporated within hours or days of application. At the other extreme, other active ingredients have a very low vapour pressure and are not subject to photodegradation, so can remain on the soil surface for days and possibly even weeks without significant loss from these pathways.

Incorporation usually takes one of four forms:

- **Full cut mechanical incorporation.** Prior to the advent of reduced tillage, this was the major incorporation method used in Australia and involved a light to moderate mechanical cultivation, usually with harrows or offset discs. This form of incorporation works well for highly volatile products such as trifluralin and tri-allate, provided it is done within hours of the spray application. Historically it was common to see harrows being towed directly behind the boomspray, or operating in the same paddock while spray application was still underway.
- **Incorporation by sowing (also commonly referred to as IBS).** This tactic is used extensively in reduced and zero till farming systems. A knife point seeder is set up to 'throw' a small amount of treated soil out of the sowing furrow and onto the inter-row to cover the herbicide which has been previously applied to the soil surface. Typically this will only work with seeders set up to plant on approximately 25 to 30cm row spacing. Careful attention to seeder set up is required to ensure even inter-row coverage while preventing throw of treated soil into the next furrow.

With some volatile herbicides (e.g. trifluralin and tri-allate), the labelled rate for IBS application is often much higher than that used in a full cut incorporation method. A higher application rate used with these herbicides in an IBS system is possible due to:

- limited mixing of the treated soil which means there is greater separation between the herbicide band near the soil surface and the crop seed
- increased binding to retained stubble
- much of the herbicide above the crop row is removed and displaced into the inter-row area, and
- incomplete soil coverage of the herbicide which often results in greater volatility losses.

These factors reduce the potential for contact between the herbicide and the emerging crop.

- **Irrigation.** If overhead irrigation is available, then this can be used to incorporate some herbicides. The volume of water required will depend upon the soil type, ground cover, solubility of the herbicide and the existing soil moisture. Typically a 5 to 10mm irrigation event is usually satisfactory for herbicide with higher solubility, while 20 to 50mm may be required for herbicides with 'low' solubility. It is important not to over water and risk moving the herbicide down the soil profile before binding has occurred.

Other forms of irrigation such as furrow irrigation are not recommended for herbicide incorporation. This is due to unevenness of soil wetting between the start and finish of the furrow; too much irrigation water is usually applied; runoff into tail ditches; and the fact that furrow irrigation also wets along a horizontal front. Also, herbicide located on the top of irrigation furrows is only incorporated by capillary action from below (sometimes referred to as 'subbing-up'). This may lead to an inadequate level of herbicide incorporation in these zones.

- **Rainfall** is often relied on and used for incorporation, especially in fallow situations. In this case, applications should be made prior to a forecast rainfall event. As forecasts do not always eventuate and rainfall volume can be highly variable, this practice can lead to inconsistent results.

In situations where incorporation is advisable, the objective is to move the herbicide into the top few centimetres of soil where it will be protected from UV degradation and volatilisation, yet still keeping it in the zone required for weed control (which is often close to the soil surface for shallow germinating weeds, especially in zero till systems).

## Herbicide behaviour in the soil

Once a pre-emergent herbicide is in the soil, an equilibrium is established between how much is bound to clay and organic matter and is therefore less available for plant uptake; and how much is dissolved in the soil water and available for root uptake. Factors that affect the degree of binding are the soil type (structure, pH and cation exchange capacity); organic matter in the soil; the solubility of the compound; the amount of available soil moisture; and the inherent binding strength of the molecule.

### Position of the herbicide in the soil

The location of targeted weed seeds is an important consideration. In a zero till environment, most weed seed is likely to be located on or near the soil surface. In a zero till system, it is most likely that pre-emergent herbicides that bind and stay relatively close to the soil surface in the zone where the weed seeds are germinating will be preferred.

Conversely, if deeper germinating weeds are the target, then having a herbicide which stays tightly bound to the soil surface may allow weeds to germinate at depth and be able to grow through the herbicide band on the soil surface.

**For more information on how zero/minimum till farming influences pre-emergent herbicides**

**https://www.youtube.com/embed/s63GYYyflzw?start=48&end=113**

A practical example of this would be where trifluralin is used on annual ryegrass.

In a tilled system, ryegrass seed is spread through the soil surface to the depth of tillage. When trifluralin was applied at or prior to sowing and harrowed in, it was also mixed in this zone. This diluted the trifluralin throughout the surface zone. At the rates that could be used weed control would often be marginal. Crop damage was also a concern, as the trifluralin treated zone was often close to, or just above, the depth of the crop seed.

In modern no-till systems, weed control using trifluralin via 'incorporate by sowing' (IBS) application often results in higher levels of control than in traditional tilled systems with full incorporation. In a no-till system, ryegrass seeds are concentrated on or near the soil surface, as is the herbicide. Higher rates can be applied as the margin for crop selectivity is larger than in a full mechanical incorporation system, due to greater spatial separation between the narrow herbicide band at the soil surface and the deeper cereal seed. Also, the herbicide over the row is displaced into the inter-row at sowing - further enhancing crop selectivity, while also reducing volatilisation loss of the herbicide.

### Soil texture and cation exchange

The type of soil often has a significant bearing on the performance of the pre-emergent herbicide. Soil texture (the ratio of sand, silt and clay) and soil organic matter will have an effect on the binding ability of the herbicide (adsorption). Cation exchange capacity (CEC) is used as a measure of the soils' adsorption sites where binding can occur.

Heavier clay soils and soils with higher organic matter have more binding sites (higher CEC) and can bind more herbicide. Increased binding is likely to result in higher application rates being required to achieve a given level of weed control, as less herbicide is available in the soil water for uptake by germinating weeds. Increased binding also generally results in less leaching.

Conversely, in sandy or low organic matter (lower CEC) soils, there is less binding with more herbicide likely to be available in the soil water. This may lead to increased risk of injury to crops soon after application where there is a lot of freely available herbicide in the soil water, especially for highly soluble herbicides. As a result, many labels recommend a lower application rate in lighter soils.

Duplex soils with a sandy shallow topsoil over a heavier B horizon can be particularly challenging. Low binding and high availability may apply in the A horizon, but strong binding and therefore persistence of the herbicide may occur in the B horizon. This can lead to high levels of exposure to the crop early, with long lived persistence for some products.

## Herbicide properties affecting soil binding and availability

### Solubility

Solubility is a measure of how much herbicide can dissolve in water, an important consideration with regard to incorporation by rainfall or irrigation and uptake by the germinating weeds. Solubility is usually quoted in mg/L of water at 20°C.

**For more information on how solubility affects pre-emergent herbicides**

**https://www.youtube.com/embed/s63GYYyflzw?start=478&end=573**

Herbicides with low water solubility often require larger volumes of rainfall to achieve incorporation and tend to be less available in the soil moisture than more soluble products. Typically, for optimum performance, herbicides with low solubility need good moisture conditions after application and also for the period of desired weed control.

Conversely, herbicides with high solubility are relatively easy to incorporate with limited rainfall. They generally prefer to remain in the soil moisture phase where they are more freely available to the plant or weed. However, if the herbicide is highly soluble it will have a tendency to move with the soil moisture, and be more likely to leach or cause off target effects.

## Binding

When a herbicide is incorporated into the soil, a percentage will bind to the soil organic carbon and soil particles.

The degree of binding can be predicted by considering the Soil/Water Adsorption Coefficient ($K_d$). The $K_d$ value is the ratio of herbicide adsorbed onto the soil in comparison to the amount remaining in the soil water. It is calculated as follows: $K_d$ = (kg herbicide/kg soil) / (kg herbicide/L water)

As binding is highly influenced by the level of organic matter, the binding coefficient is often normalised to take into account organic carbon levels in different soils and is presented as a $K_{oc}$ value. The $K_{oc}$ value is calculated by the equation:

$K_{oc} = K_d$ / soil organic carbon

The higher the $K_{oc}$ value, the more tightly the herbicide is bound. Herbicides with a low $K_{oc}$ are less tightly bound to the soil and more freely available in the soil water. As a result, they have greater capacity to move with the soil water, especially in sandy soil or soils with low organic matter.

**For more information on how binding affects pre-emergent herbicides**

**https://www.youtube.com/embed/s63GYYyflzw?start=602&end=779**

For some molecules the $K_{oc}$ is very sensitive to soil pH, in particular the imidazolinone herbicides which bind tighter at acidic (low) pH.

As soil factors may have a significant bearing on the level of binding, $K_{oc}$ will often be reported as a range (usually with an average across trials), especially where the range is broad.

**Table 4: Examples of solubility of selected pre-emergent herbicides.**

| Active ingredient (Herbicide) | Solubility (mg/L@ 20°C)[^] | |
|---|---|---|
| diflufenican (Brodal®) | 0.05 | Low solubility (0 to 49 mg/L @20°C)<br>Likely to require moist conditions for incorporation and uptake |
| trifluralin (Treflan®) | 0.22 | |
| pendimethalin (Stomp®) | 0.33 | |
| flumioxazin (Terrain®) | 0.8 | |
| pyroxasulfone (Sakura®) | 3.5 | |
| tri-allate (Avadex®) | 4 | |
| simazine (Gesatop®) | 5 | |
| isoxaflutole (Balance®) | 6 | |
| terbuthylazine (Terbyne®) | 7 | |
| propyzamide (Rustler®) | 9 | |
| prosulfocarb (Arcade®) | 13 | |
| atrazine (Gesaprim®) | 30 | |
| diuron (various) | 36 | |
| metazachlor (Butisan®) | 450 | Moderate solubility (50 to 500 mg/L @20°C) |
| s-metolachlor (Dual®) | 480 | |
| picloram acid (Tordon®) | 560 | High solubility (> 501 mg/L @ 20°C) |
| triasulfuron (Logran®) | 815 | |
| metribuzin (Sencor®) | 1100[#] | |
| dimethenamid-P (Outlook®) | 1499 | |
| imazapic (Flame®) | 2230 | |
| clopyralid acid (Lontrel®) | 7850 | |
| chlorsulfuron (various) | 12500 | |

[^] University of Hertfordshire. (2006-2019). The Pesticide Properties DataBase (PPDB) developed by the Agriculture & Environment Research Unit (AERU), University of Hertfordshire, Accessed on 2nd October 2019 http://sitem.herts.ac.uk/aeru/iupac/index.htm

[#] Shaner, D. (2014). Herbicide Handbook (10th Edition) Weed Society of America

## Table 5: Examples of average adsorption coefficients for selected pre-emergent herbicides.

| Active ingredient (Herbicide) | Average $K_{oc}$ value^ | | |
|---|---|---|---|
| pendimethalin (Stomp®) | 17 491 | $K_{oc}$ > 5000 Non-mobile. | Likely to bind tightly to soil and organic matter |
| trifluralin (Treflan®) | 15 800 | | |
| tri-allate (Avadex®) | 3 034 | $K_{oc}$ 500 to 5 000 Slightly mobile | |
| diflufenican (Brodal) | 1 622-2 369[#] | | |
| prosulfocarb (Arcade®) | 1367-2340[#] | | |
| flumioxazin (Terrain®) | 889 | | |
| propyzamide (Rustler®) | 840 | | |
| diuron (various) | 680 | | |
| terbuthylazine (Terbyne®) | 230[@1] | $K_{oc}$ 75 to 500 Moderately mobile | More likely to move with soil water |
| pyroxasulfone (Sakura®) | 223 | | |
| dimethenamid-P (Outlook®) | 218[@1] | | |
| s-metolachlor (Dual®) | 200[#] | | |
| isoxaflutole (Balance®) | 145 | | |
| imazapic (Flame®) | 137 | | |
| simazine (Gesatop®) | 130 | | |
| atrazine (Gesaprim®) | 100 | | |
| metribuzin (Sencor®) | 60[@1] | $K_{oc}$ 20 to 75 Mobile | |
| triasulfuron (Logran®) | 60 | | |
| metazachlor (Butisan®) | 54 | | |
| chlorsulfuron (various) | 40[#] | | |
| picloram (Tordon®) | 13 | $K_{oc}$ 0 to 20 Very mobile | |
| clopyralid (Lontrel®) | 5 | | |

^ University of Hertfordshire. (2006-2019). The Pesticide Properties DataBase (PPDB) developed by the Agriculture & Environment Research Unit (AERU), University of Hertfordshire. Accessed on 2nd October 2019 http://sitem.herts.ac.uk/aeru/iupac/index.htm

[#] Shaner, D. (2014). Herbicide Handbook (10th Edition) Weed Society of America

[@1] USDA Natural Resources Conservation Service. Windows Pesticide Screening Tool

To understand how this affects interaction in the soil, compare the solubility (Table 4) and average $K_{oc}$ values (Table 5) for the commonly used Group C herbicides atrazine and diuron. Both atrazine and diuron have similar (and low) solubility. However the adsorption coefficient for diuron is significantly higher, indicating that it will bind much tighter to the soil and organic matter at the soil surface, and hence it is effective on many small seeded surface germinating weeds. Conversely, atrazine is more loosely bound to the soil and will move further down the profile with the wetting front after a rainfall event. Therefore, what is often observed is that atrazine can provide reasonable levels of control of surface germinating weeds if there is just enough rainfall to incorporate the herbicide, but not too much to move it deeper in the profile. With additional rainfall, atrazine will move further down the soil profile, often into a 5 to 10cm zone where many larger seeded broadleaf weeds germinate. Atrazine frequently performs better against these larger seeded / deeper germinating targets than diuron, which is more tightly bound and more likely to be in the top 0 to 2cm zone.

## Soil moisture

Free soil moisture is critical to the performance of most pre-emergent herbicides. With low available soil water, pre-emergent herbicides that rely on root uptake will be less available.

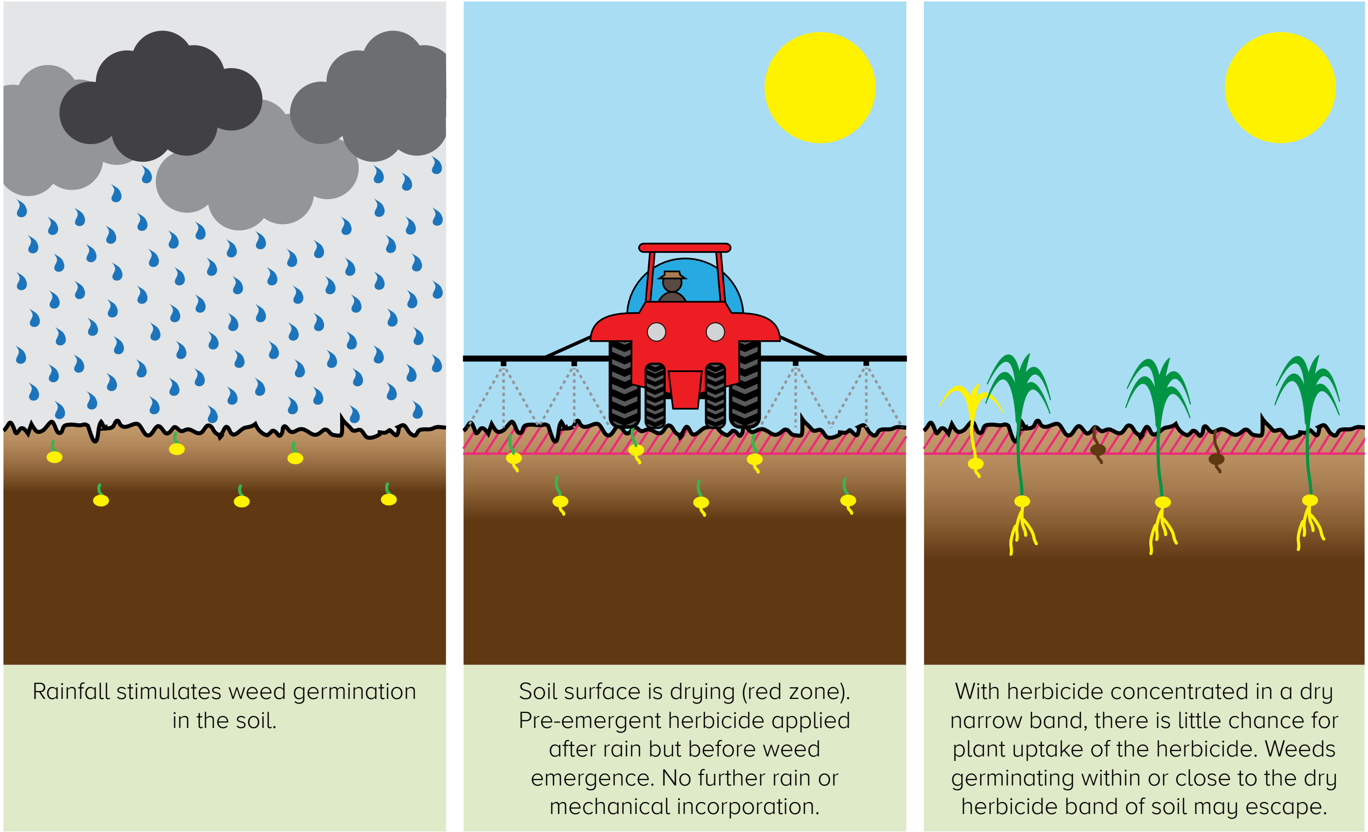
For herbicides with low solubility, lower levels of herbicide will be dissolved in the available soil water than for herbicides with higher solubility. In situations of high available soil moisture, weeds take up adequate soil moisture containing herbicide, even where herbicide solubility is low. However, where soil water is low there may be insufficient herbicide entering the plant with these low soluble herbicides.  This is why many low soluble, pre-emergent herbicides may fail to provide good weed control under dry or 'lower soil water" conditions. To maximise performance of low-solubility herbicides, good soil moisture is required, both for incorporation and for the desired period of weed control.

Once in the soil, the herbicide establishes an equilibrium between the amount available in the soil water and that binding onto soil colloids and organic matter. After a herbicide is incorporated, it typically takes several days for this equilibrium to establish. Most new herbicide labels will generally have a constraint to the effect of 'Do not irrigate' or 'Do not apply if runoff rainfall is expected' within 2 or 3 days after application. This is partially to allow time for soil binding to take place and the equilibrium to be established.

Once an equilibrium is established, it is an active process with herbicide constantly sorbing or desorbing from binding sites in ratios defined by its binding coefficient values.

A worst case scenario for pre-emergent herbicide efficacy is depicted below (Figure 4). The solution is generally to apply the pre-emergent herbicide before a rain front, rather than immediately after one.

**Figure 4:** Dry topsoil with inadequate soil water to allow herbicide uptake by emerging weeds – the perfect storm for weed escapes.


Rainfall stimulates weed germination in the soil.

Soil surface is drying (red zone). Pre-emergent herbicide applied after rain but before weed emergence. No further rain or mechanical incorporation.

With herbicide concentrated in a dry narrow band, there is little chance for plant uptake of the herbicide. Weeds germinating within or close to the dry herbicide band of soil may escape.

## Breakdown

Once in the soil, herbicide breakdown typically occurs via microbial degradation or chemical reactions such as hydrolysis.

For many herbicides, microbial degradation is the primary path of degradation. Conditions that encourage soil microbes (warm soils, good soil moisture, adequate oxygen, organic matter, nutrients and neutral pH) will typically see faster degradation and shorter persistence of the herbicide.

Rainfall in summer, when conditions are warm, will lead to much higher microbial populations than rainfall in the colder months. Extended dry periods which do not support the sustained activity of microbial populations can substantially increase the persistence of these herbicides. If the top 10-15cm of soil is not moist, then little herbicide degradation is occurring, regardless of how many months have passed.

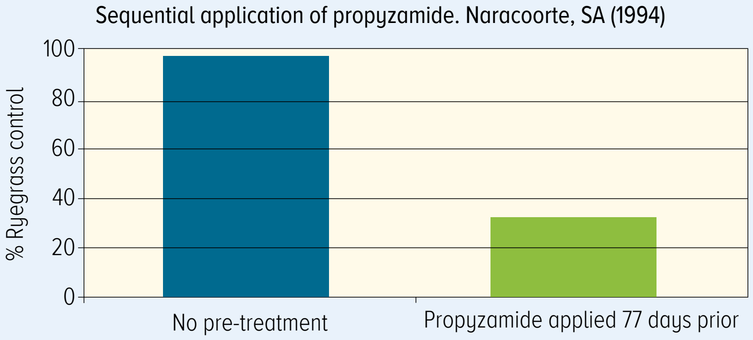
Many labels will have a plantback period specifying the number of months and a rainfall requirement from application until susceptible crops can be sown. Rather than considering the rainfall in total, it is better to think in terms of number of weeks of moist topsoil. A single rainfall event with months of dry topsoil is less effective at sustaining

## Enhanced microbial degradation

For some residual herbicides that are broken down by microbes, accelerated degradation has been reported where the herbicide has been applied frequently to the same soil. Atrazine (Group C) and propyzamide (Group D) are two examples that have been widely reported in the literature.

For example, a 1994 trial conducted at Naracoorte, South Australia (Figure 5) showed that control of ryegrass declined significantly from a second application of propyzamide in the same season.

**Figure 5:** Effect of sequential applications of propyzamide on ryegrass. Adapted from Hole, S., & Powles, S. (1997).



Numerous studies demonstrating enhanced microbial degradation of atrazine under a range of agricultural situations have been published Popov, V., Cornish, P., Sultana, K., & Morris, E. (2005); Mandelbaum, M., Sadowsky, M., & Wackett, L. (2008).

Should accelerated degradation occur in the field, the length of residual weed control will be reduced. This may also have an impact on plantbacks to rotation crops.

microbial populations compared to the same rainfall occurring as a number of events that keep the topsoil wet for longer.

A mobile herbicide (high solubility/low binding) that is only degraded by microbes may persist for long periods deeper in the soil profile where there is little microbial activity. Good examples of this are the Group I pyridines (e.g. picloram, clopyralid) and the Group B imidazolines and sulfonylureas. These herbicides can carry over to following seasons and affect rotational crops when the crops roots get down to access the herbicide at depth.

In deep, free draining soils, these mobile herbicides may be moved deeper in the profile following each major rainfall or irrigation event, potentially moving out of the crop root zone of the following crop. However, problems often arise with mobile herbicides where there is a soil change, pH change or some other structural limitation that causes the herbicide to concentrate at depth and prevents further leaching.

Soil pH generally does not have a large impact on the persistence of most herbicides where the primary breakdown pathway is via microbial degradation. However, there are exceptions. One exception is the imidazolinones where the strength of binding is strongly influenced by soil pH. The bioavailability of imidazolinones is increased in higher pH (alkaline) soils and this higher availability in solution also makes imidazolinone herbicides more available for microbial degradation. In low pH (acidic) soils, binding of imidazolinones increases, thus reducing bioavailability to plants and weeds and also to the microbes required for breakdown, resulting in increased persistence at acidic pH.

For herbicides that breakdown via hydrolysis (a chemical reaction), the speed of breakdown is influenced by temperature, moisture and is often highly influenced by pH. The Group C sub-group of triazines and the Group B sub-group of sulfonylureas typically undergo chemical hydrolysis in neutral or acid soils. However, the speed of this reaction decreases (or ceases) as pH increases. Under high pH (alkaline conditions), breakdown then occurs via the slower process of microbial degradation, so they persist much longer in alkaline soils.

Particular problems are often seen with triazines and sulfonylureas in duplex soils that have an alkaline and impermeable sub-soil. In these soils, herbicide that is moved deeper in the profile encounters the alkaline sub-soil, where hydrolysis is slow or does not occur. At this depth there is generally minimal microbial activity, so these herbicides can persist for multiple years in these situations.

As a herbicide is lost to the system (broken down by microbes or hydrolysis, taken up by plants or leached down the profile), the equilibrium between the herbicide in the soil and the water phase will remain in the same ratio (as determined by the $K_d$ value of the herbicide). Typically, this means that the balance of sorption/desorption will see some of the herbicide that was bound to the soil particles gradually released back into the soil water (desorption) to keep the ratio (sorbed/desorbed) constant.

In this way, residual herbicides provide extended periods of weed control. After the herbicide has been incorporated into the soil, a portion of the herbicide binds to soil and organic matter and some is freely available in the soil water. Herbicide is lost from the soil water phase (degradation, leaching, taken up by plants) and this is then 'replenished' over time from herbicide previously bound to the soil and organic matter that is released back into soil solution.

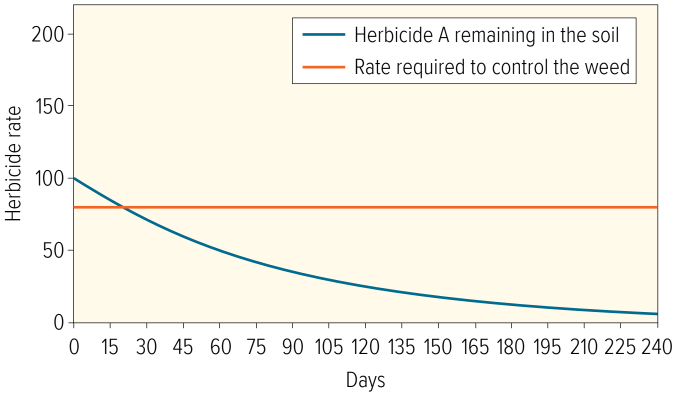
## Persistence

How long a herbicide remains in the soil can be highly variable and depends upon the soil type (binding), temperature, water, organic matter, speed and type of breakdown and application rate.

The rate of herbicide persistence is usually reported as a $DT_{50}$ value. The $DT_{50}$ value is a half-life, or the days of time that it takes for 50% of the herbicide in the soil to breakdown. The rate of breakdown varies between different soils and environmental conditions, so the $DT_{50}$ is often reported as a range of values, or an average, or both.

In the example following (Figure 6), a moderately persistent theoretical Herbicide A (blue line) has a $DT_{50}$ value of 60 days. As can be seen from the graph, if 100 units are applied then after 60 days, 50 units will be remaining. After a further 60 days, 25 units remain. If it takes 80 units of the herbicide to effectively control the target weed (orange line) it can be seen that Herbicide A will provide approximately 20 days of residual control before there is insufficient herbicide remaining to provide ongoing control.

**Figure 6:** Persistence over time of a moderately persistent herbicide ($DT_{50}$ = 60 days).



Molecules with a $DT_{50}$ under 30 days are often classified in herbicide literature as 'non-persistent' as they tend to breakdown relatively quickly. However, these herbicides classified as 'non-persistent' ($DT_{50}$ less than 30) can still be useful pre-emergent herbicides if applied at a high enough rate to allow them to provide the desired length of residual control.

The graph following (Figure 7) includes an example of theoretical Herbicide B - a 'non-persistent' herbicide that has a $DT_{50}$ of 15 days. Should Herbicide B also require 80 units to control the weed, then it is also possible to obtain the same length of effective residual control by applying a higher starting dose (green line). A number of pre-emergent herbicides used in the Australian grains industry achieve their stated level of residual control by utilising this concept of high application rates to counter the rapid breakdown.

## Table 6: Examples of average DT$_{50}$ values for selected pre-emergent herbicides.

| Herbicide | Average DT$_{50}$ value^ | | |
|---|---|---|---|
| dimethenamid-P (Outlook®) | 7 (2-16) | DT$_{50}$ 0 to 30 Non-persistent | Often have minimal plantback constraints, unless the rotational crop is highly sensitive. |
| metazachlor (Butisan®) | 7 (3-21) | | |
| prosulfocarb (Arcade®) | 10 (7-13) | | |
| flumioxazin (Terrain®) | 18 (16-20) | | |
| metribuzin (Sencor®) | 19 (14-28[#]) | | |
| s-metolachlor (Dual®) | 21 (11-31) | | |
| pyroxasulfone (Sakura®) | 22 (16-26) | | |
| terbuthylazine (Terbyne®) | 22 (6-149) | | |
| chlorsulfuron (various) | 36 (10-185) | DT$_{50}$ 30 to 100 Moderate | Plantback periods will depend on the sensitivity of the following crop. |
| triasulfuron (Logran®) | 39 (16-92) | | |
| clopyralid acid (Lontrel®) | 40 (12-70)[#] | | |
| tri-allate (Avadex®) | 46 (8-205) | | |
| propyzamide (Rustler®) | 60[@7] (18-53[#]) | | |
| atrazine (Gesaprim®) | 60[@1] (6-108) | | |
| diuron (various) | 90[#] | | |
| simazine (Gesatop®) | 90 (27-102) | | |
| picloram acid (Tordon®) | 90 (20-300)[#] | | |
| pendimethalin (Stomp®) | 100 (40-187) | | |
| trifluralin (Treflan®) | 170 (35-375) | DT$_{50}$ >100 Persistent | Plantback constraints will often occur.<br>Long re-cropping intervals will exist to sensitive crops. |
| imazapic (Flame®) | 232 (31-410) | | |
| diflufenican (Brodal) | 105-210[#] | | |

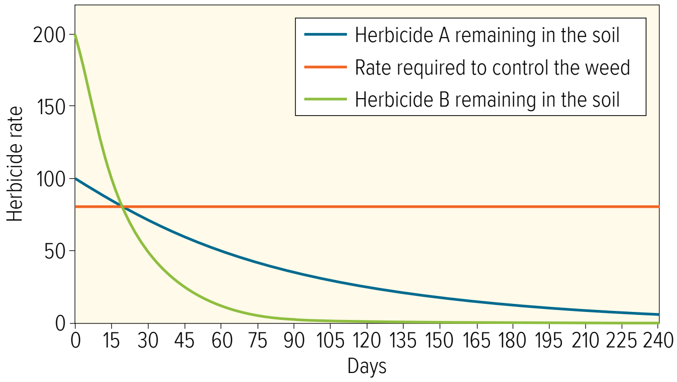
^ University of Hertfordshire. (2006-2019). The Pesticide Properties DataBase (PPDB) developed by the Agriculture & Environment Research Unit (AERU), University of Hertfordshire. Accessed on 2nd October 2019 http://sitem.herts.ac.uk/aeru/iupac/index.htm

[#] Shaner, D. (2014). Herbicide Handbook (10th Edition) Weed Society of America

[@1] USDA Natural Resources Conservation Service. Windows Pesticide Screening Tool

[@7] Imtrade. (2017). Edge 900WG Safety Data Sheet

**Figure 7:** Comparison of a short (DT$_{50}$ = 15 days) and a moderately persistent herbicide (DT$_{50}$ = 60 days) over time.



## Rotational crop constraints (plantbacks)

By definition, all pre-emergent herbicides, even those classified as non-persistent, usually have some level of plantback constraint to susceptible crops.

Products that rely on microbial breakdown for degradation require an environment where soil organisms are active for prolonged periods of time. As a biological process, it takes time with adequate soil moisture and temperature for a microbial population to build – a process that is unlikely to occur under hot, dry soil conditions. Often, the amount of total rainfall is less important to microbial breakdown than how long the topsoil, which contains most of the microbes is moist for.

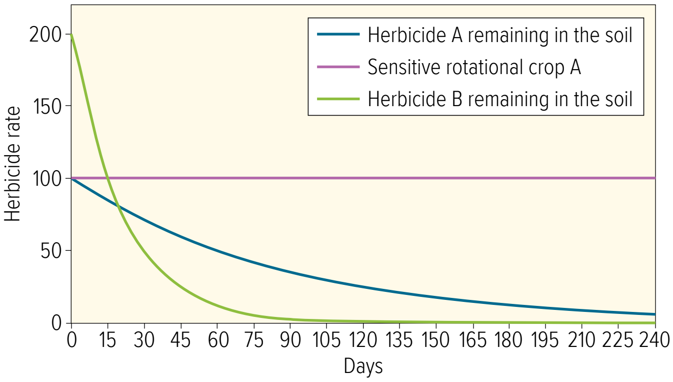
NSW DPI publications *Weed Control in Summer Crops* and *Weed Control in Winter Crops* (page 43) provide detailed tables of plantback periods for most pre-emergent herbicides used in grains production in Australia. These tables are relevant to NSW soils and may be different for some products in different states.

ALWAYS check and follow the rotational crop advice on the product label.

Using the example shown in Figure 7, where the use patterns of Herbicide A and Herbicide B were both established to provide a similar length of residual control of the target weed (approximately 20 days), the safe plantback period to a susceptible rotation crop can vary significantly.

In Figure 8, theoretical rotational crop A can tolerate 100 units of either herbicide (purple line). Therefore, as this rate is the starting application rate of Herbicide A, there is effectively no plantback limitation for this crop at this application rate of Herbicide A, despite Herbicide A being a moderately persistent product. However, in this example it can be seen that there would be a short, 2 to 3 week plantback to Herbicide B, due to the higher initial application rate, despite Herbicide B being the less persistent product.

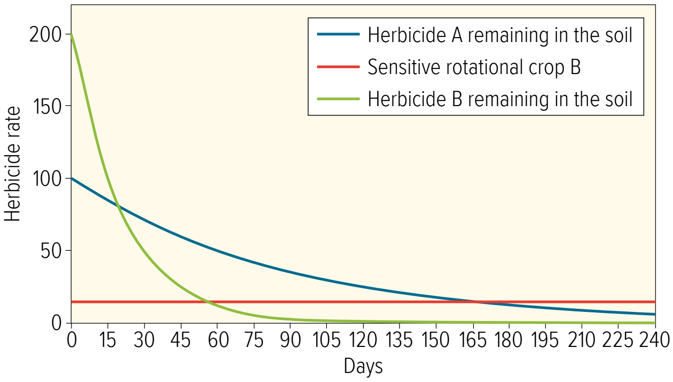
**Figure 8:** Hypothetical comparison of a short ($DT_{50}$ = 15 days) and a moderately persistent herbicide ($DT_{50}$ = 60 days) over time relative to a sensitive rotational crop.



However, for these same two theoretical herbicides used in the figures above, a different outcome may be observed if the rotational crop is highly sensitive. In Figure 9, sensitive rotational crop B (red line) can only tolerate 15 units of either herbicide. This example would indicate that rotational crop B could only be sown approximately 60 days after application of the relatively non-persistent Herbicide B.

However, if the sensitive rotational crop B is to be grown after application of Herbicide A, then a plantback of approximately 170 days would be required, in this example.

**Figure 9:** Comparison of a short ($DT_{50}$ = 15 days) and a moderately persistent herbicide ($DT_{50}$ = 60 days) over time relative to a sensitive rotational crop.



***Note:** These hypothetical examples demonstrate the principle of how application rate, speed of herbicide breakdown and crop/weed sensitivity affects the length of observable symptoms. In practice, different soil types and environmental conditions will vary the speed of breakdown for any herbicide. It is also probable that different species will have different tolerances to each herbicide, unlike the simplified example above.*

*Any additional stress on germinating weeds or rotational crops will also affect the tolerance of the species to remaining levels of herbicide residue in the soil.*

*Herbicide manufacturers undertake extensive testing of rotational crops under a range of different environmental conditions and soil types when developing rotational crop recommendations. Always follow the advice on product labels and other supplementary information provided by the manufacturer.*

Product labels are designed to cater for typical situations and hence should be followed. However, they may not cover all situations and extremes. In borderline situations, the following strategies may provide additional data on which to assess or reduce risk:

- Soil testing may be possible from a laboratory specialising in herbicide residue testing. This can be time consuming, expensive, and testing may not be available for all herbicides. Sampling depth will also be important. Additionally, test results will only reveal the quantity of herbicide remaining in the soil as measured by the protocol used by that laboratory. If levels of herbicide are detected, then this will require interpretation to understand if this level will prevent establishment or healthy growth of the desired crop. Data to help interpret test results is limited and often hard to find. For highly active herbicides it could be possible that the laboratory testing protocol may not be sensitive enough to detect quantities that will still damage some rotational crops.
- A simple bioassay can be conducted whereby seeds of the desired crop are sown into the field a few weeks prior to the desired sowing date and establishment is observed to understand the likely level of crop injury. This can give a quick indication as to likelihood of any residues affecting emergence. However care must be taken, especially with herbicides that are more mobile and may have moved down the soil profile. In this situation, germination may be unaffected; however severe damage or plant death could still result when the roots of the new crop extend into the residual herbicide layer further down the profile. Also, some herbicides at sub lethal doses may not greatly affect emergence, but may significantly reduce biomass after emergence. As such, emergence tests can provide false confidence.
- Aggressive cultivation prior to sowing of a sensitive crop is recommended on the label of some herbicides, typically those that are tightly bound to the soil surface. This may dilute the remaining herbicide throughout the soil profile, allowing improved crop establishment – however this is a risky process to rely on.
- Switch to a crop variety or crop type that is tolerant to the expected herbicide residue.
- Avoid applications at sowing or early post-emergent from the same herbicide mode of action group that was used in the preceding crop or fallow, as this may 'top up' soil residues.
- Use good agronomy to promote early crop health and vigour and avoid using any practice that might add an additional plant stress to the crop.

# CROP SAFETY

The safety of grain crops sown pre or post application when using a pre-emergent herbicide is an important consideration.

There are a number of strategies that can help achieve acceptable crop safety. These include:

**Crop tolerance.** Some crops are inherently more tolerant to a particular herbicide. Usually this tolerance comes from the crop being able to rapidly detoxify that herbicide. There may also be differences between individual varieties in their ability to detoxify a particular herbicide.

An example is the use of chlorsulfuron in wheat. Wheat can quickly detoxify chlorsulfuron via metabolic processes, however if the crop is not metabolising due to waterlogging or frost, severe crop symptoms can appear as the crop is unable to detoxify the herbicide fast enough.

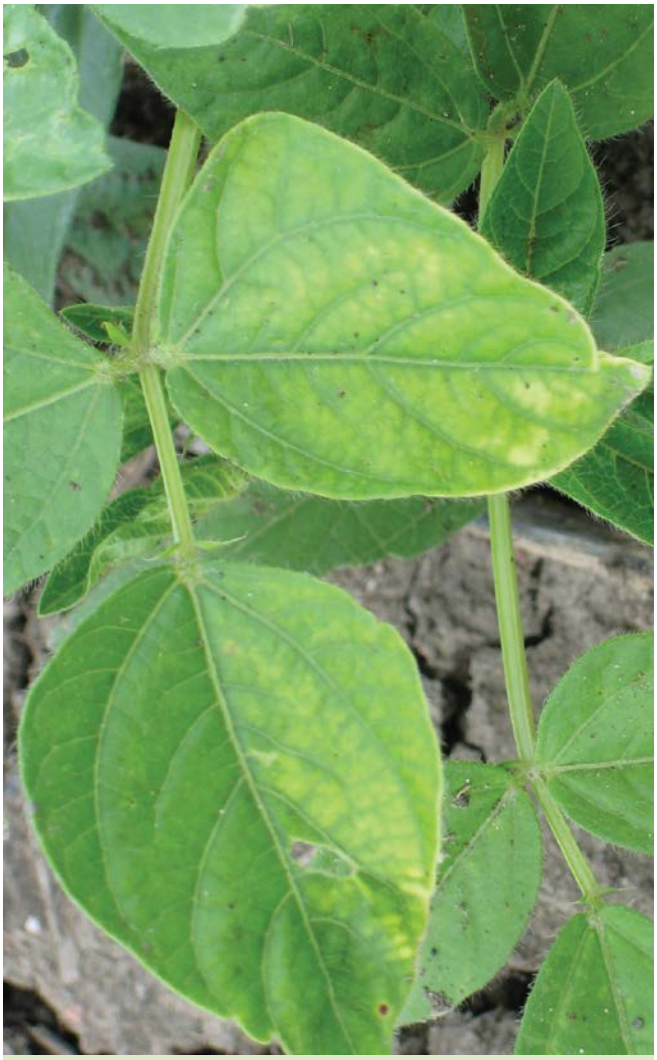
In some situations a herbicide safener may be able to be used to further accelerate the crops ability to metabolise the herbicide. A good example of this is the application of Concep® II to sorghum seed to accelerate the metabolism of s-metolachlor.

Some crop varieties have been bred to include tolerance to specific herbicides. An example are Clearfield® varieties that express tolerance to imidazolinone herbicides. This enables the use of a particular herbicide mode of action within those crops that would otherwise be lethal. It also provides rotational options in the event of a previous herbicide residue from that chemistry group remaining in the soil at sowing.

**Differential placement.** A herbicide that is toxic to the crop may still be able to be used where it can be spatially separated from the crop. If the herbicide binds sufficiently to the soil surface, it may be able to be used in a situation where the crop is sown at a depth below the herbicide band. While this may be an effective strategy for some herbicides, crop injury may still occur in situations where herbicide is moved down into or below the crop seed zone, particularly if heavy rainfall occurs as the first incorporating rainfall. Crop damage is often a function of one or more of the following: shallow seeding depth, herbicide placement in (or non-removal from) the crop row, heavy rain after sowing, soil with low binding characteristics and/or products with high solubility and/or low binding.

**Physical removal of herbicide in the furrow.** The incorporation by sowing (IBS) technique used in conjunction with knife point seeders can achieve adequate selectivity for some product/crop combinations. This is achieved by physically removing the treated soil directly above the furrow and throwing this into the inter-row, leaving an untreated area through which the crop can emerge. Pay careful attention to seeder set up to ensure that treated soil is not thrown into adjoining crop rows. Press wheels generally help to minimise treated soil from falling back into the furrow. Heavy rainfall after application can still cause problems if treated soil is washed into the furrow.

Regardless of the strategy employed, there may be times when an adverse crop effect still occurs when crop placement and environmental conditions allow some herbicide / crop contact. Frequently situations of crop damage coincide with the emerging crop seedling being under additional stress that slows the rate of metabolism, reducing the crop's ability to detoxify the herbicide. This is often observed in situations of waterlogging or prolonged cold or frost.



Waterlogging in combination with pre-emergent herbicides may sometimes cause crop injury.
Photo: Mark Congreve

# IN SUMMARY

To understand how a pre-emergent herbicide will behave in the farming system, the following points should be known:

- **What weeds are in the paddock and where are the seeds?** Knowing what is in the weed seedbank and where these seeds are located (i.e. mainly on the surface or distributed in the top 10cm) will be important in selection of the herbicide to be used and will assist in setting realistic expectations for control.
- **Is the herbicide subject to volatilisation or photodegradation?** Knowing this will determine the incorporation strategy required to minimise loss to the environment.
- **How soluble is the herbicide?** This will influence how much rain is required for incorporation and to wash off stubble; how easily it will be taken up by the germinating weed and crop; and susceptibility to moving deeper into the soil profile with soil water (or off-site in runoff), potentially causing crop injury or being lost to leaching.
- **What is the soil type and level of organic matter?** Sandy or low organic matter soils (low CEC) have fewer binding sites. Other factors being equal, more herbicide will be available for crop and weed uptake in lighter soil types than in a heavier or higher organic matter soil.
- **How tightly does the herbicide bind to soil and organic matter?** Herbicides that bind tightly generally stay close to where they are applied (unless the soil moves) and will persist for longer. They will also be more difficult to wash off stubble.
- **What is the soil pH?** The pH affects how long some herbicides persist for and how available they are for plant uptake and soil binding.
- **How persistent is the herbicide and how does it breakdown?** This will give an indication of the expected length of residual control and plantback constraints to sensitive crops.
- **Rainfall and temperature:** Rainfall after application is important for incorporation and to allow the herbicide to be available for root uptake. Rainfall and temperature also affect degradation.
- **Application rate:** Choice of application rate will affect the efficacy, length of effective residual and possibly crop selectivity.
- **Product labels:** Product labels are developed to reflect how herbicides behave in the soil. Always read and follow product label directions.

# KEY RESIDUAL HERBICIDES

Some commonly used pre-emergent herbicides and their chemical properties are discussed in this section. This information assists in understanding why they behave as they do and what considerations are important in their performance as a pre-emergent herbicide.

For herbicides not covered in detail in this section, Table 7 lists the important properties of the majority of pre-emergent herbicides used in Australian grain production[2]. Readers should be able to interpret these properties in relation to the principles outlined in the initial chapters of this manual and therefore understand which drivers are most likely to be important for any particular herbicide and situation.

Unless otherwise stated, values quoted are specific to the active ingredients in the tables below and were sourced from the Pesticide Properties Database which can be found at http://sitem.herts.ac.uk/aeru/iupac/index.htm University of Hertfordshire. (2006-2019). The Pesticide Properties DataBase (PPDB) developed by the Agriculture & Environment Research Unit (AERU), University of Hertfordshire. Accessed on 2nd October 2019.

## GROUP A

**Mode of action:** Group A herbicides inhibit the acetyl CoA carboxylase (ACCase) enzyme which blocks fatty acid synthesis within the plant. ACCase is most active in meristematic regions of the young plant where new cell growth is occurring. As a result, Group A herbicides are most effective on young weeds. Cell production ceases almost immediately, however it is typically 1-2 weeks before symptoms are visible.

There are three sub-groups of Group A herbicides used in Australian grain production. These are:

- Aryloxyphenoxypropionates (fops),
- Cyclohexanediones (dims), and
- Phenylpyrazoles (dens).

Multiple different target site mutations and non-target site mechanisms for resistance to Group A herbicides exist. These confer different levels of cross resistance within and between herbicides in the three Group A sub-groups. Resistance arising from an altered target site mutation is very common within Group A herbicides and high levels of resistance are common in many grass species within Australia. Incidence of non-target site resistance is present and increasing – particularly P450 enzyme-mediated metabolic resistance mechanisms. Some non-target site resistance mechanisms also confer cross-resistance to herbicides from other mode of action groups.

**General Properties:** Group A herbicides are primarily taken up by foliar adsorption and are registered for the post-emergent control of grass weeds in a range of crops and situations. They are not generally considered as pre-emergent herbicides. They have been referenced here and in Table 7 (see page 38) as some herbicides from this group do have a level of soil activity, resulting in plantback constraints.

Breakdown of the 'dim' herbicides occurs via microbial degradation and is often relatively fast, with generally less residual activity than for 'fop' herbicides. Plantback constraints to monocot crops are normally measured in weeks for the 'dims' but are often poorly defined on product labels, as typical use patterns are early in crop and there has historically been little need to define re-cropping intervals more accurately.

Breakdown of 'fops' typically is a two-stage process. Most 'fop's' are applied in the ester form which generally undergoes rapid hydrolysis and conversion to the acid form. Once in the acid form, microbial degradation becomes the primary breakdown pathway in the soil. The speed of breakdown varies between different fop herbicides, with some of the longer plantback constraints measured in terms of weeks or months. Conditions that favour good microbial activity, (i.e. warm and moist) will typically lead to the fastest breakdown. Refer to product labels for plantback information to sensitive crops.

## GROUP B

**Mode of action:** Group B herbicides work by inhibiting the acetolactate synthase (ALS) enzyme. ALS occurs throughout the plant, however is most active in meristematic regions of the plant where new cell growth is occurring. Group B herbicides are most effective on young weeds. Enzyme inhibition is rapid, usually within hours; however, it typically takes 1 to 2 weeks for visual herbicide symptoms to appear.

There are three sub-groups of ALS inhibitors used in Australian grain production:

- Sulfonylureas (SUs);
- Imidazolinones (Imis), and
- Triazolopyrimidines (TPs).

There can be significant differences between selectivity, spectrum of activity and binding sites between the groups and between individuals within the three groups. This is primarily due to different chemical structures allowing for different metabolic pathways. A major practical difference between groups that affects their environmental availability comes from how they are degraded under various soil pH conditions.

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[2] Several herbicides covered in Table 7 (see page 38) were included as their registered label contains plantback constraints to rotational crops, even though some of these products are generally not considered to provide substantial residual activity on weeds.

Resistance arising from an altered target site mutation is very common within Group B herbicides. Non-target site metabolic resistance is also present and increasing. High levels of resistance are widespread in many weed species within Australia.

**General properties:** Most Group B herbicides have high solubility and are weak acids, being systemic within the xylem and phloem once inside the plant. Many can enter the plant via foliar uptake so are suited to post-emergent use. However, a number of molecules from within this group also have soil residual activity, with substantial uptake via root absorption.

Most ALS inhibitor herbicides have broad-spectrum activity on dicots. Activity on monocots varies between individual herbicides, depending on the ability of the monocot species to rapidly metabolise the specific herbicide.

The persistence of different members of this herbicide group varies considerably and this differential persistence, combined with differential monocot selectivity, has seen many different Group B herbicides commercialised within the Australian grains industry.

For many of the sulfonylureas, hydrolysis is the primary breakdown mechanism. This can be relatively fast or quite slow, depending upon the individual compound. However, as the soil pH becomes alkaline this reaction slows, or stops, and then slow microbial degradation becomes the primary method of breakdown. For this reason, many sulfonylureas persist much longer in alkaline soils, where hydrolysis is very slow or does not occur.

With imidazolinone herbicides, microbial breakdown is the primary route of degradation and is typically very slow for most imidazolinones. Persistence in the soil increases with lower soil pH (acidic soils) as binding increases, making the herbicide less available for microbial breakdown.

Breakdown of triazolopyrimidines occurs via microbial degradation and can be quite fast for some molecules and moderate for others. This sub-group are generally less sensitive to soil pH than the other groups of ALS herbicides.

## Sulfonylureas

### Chlorsulfuron

| Getting to the soil | | | When in the soil | | |
|---|---|---|---|---|---|
| Solubility (mg/L) | 12 500 | High | Binding ($K_{oc}$) | 40# | Mobile |
| Volatility (mPa) | $3.07 \times 10^{-6}$ | Non-volatile | Half-life ($DT_{50}$) | 10 - 185 (av. 36) | Moderately persistent |
| Photodegradation | Negligible | | Mobility | Mobile in the soil<br>Potential to leach, especially at higher pH | |
| Breakdown | Hydrolysis cleaves the sulfonylurea bridge with the speed of breakdown increasing with lower soil pH. Microbial breakdown is slow. | | | | |

\# Shaner, D. (2014). Herbicide Handbook (10th Edition) Weed Society of America

Practical considerations:

- With volatility and photodegradation both being low, the herbicide will not breakdown rapidly on the soil surface after application.
- Solubility is high and binding to organic matter is low, assisting rainfall to wash herbicide off the stubble.
- Speed of breakdown depends on soil pH and moisture content. Plantback to sensitive crops can be very long in alkaline soils, especially under dry summer conditions. Observe label constraints for time and rainfall requirements.
- This also means the compound is freely available for root uptake and translocation once in the soil, however there is potential for leaching down the profile following large rainfall events, particularly in alkaline soils. If applied to dry soil without mechanical incorporation and followed by a significant rainfall event during emergence, there is potential for it to move down the profile and damage germinating crops.

### Metsulfuron

| Getting to the soil | | | When in the soil | | |
|---|---|---|---|---|---|
| Solubility (mg/L) | 2 790 | High | Binding ($K_{oc}$) | 35# | Mobile |
| Volatility (mPa) | $1.4 \times 10^{-8}$ | Non-volatile | Half-life ($DT_{50}$) | 7-37 (av. 13) | Non-persistent |
| Photodegradation | Negligible | | Mobility | Mobile within the soil however rapidly breaks down. | |
| Breakdown | Non-microbial hydrolysis occurs relatively rapidly, particularly at lower soil pH and higher soil moisture and temperature. | | | | |

\# Shaner, D. (2014). Herbicide Handbook (10th Edition) Weed Society of America

Practical considerations:

- With volatility and photodegradation both being low, the herbicide will not breakdown rapidly on the soil surface after application.
- Due to rapid hydrolysis, plantback constraints are often less than for some other sulfonylureas.
- Solubility is high and binding to soil is low so will be freely available in the soil. However, soil persistence is typically quite short.

### Sulfosulfuron

| Getting to the soil | | | When in the soil | | |
|---|---|---|---|---|---|
| Solubility (mg/L) | 1627 | High | Binding ($K_{oc}$) | 47[@1] | Mobile |
| Volatility (mPa) | 3.05 x $10^{-5}$ | Non-volatile | Half-life ($DT_{50}$) | 29-75 (av.45) | Non- persistent |
| Photodegradation | Can be significant | | Mobility | Will be freely available in the soil water | |
| Breakdown | Hydrolysis is the major breakdown pathway in low pH soils and can be relatively rapid.<br>In alkaline soils, breakdown via hydrolysis is slow, with microbial degradation becoming significant at higher pH levels. | | | | |

[@1] USDA Natural Resources Conservation Service.

Practical considerations:

- Losses to volatility are insignificant; however, loss to photodegradation can be significant if there is an extended period before incorporation. Labels recommend incorporation by sowing into moist soil when being used as a pre-emergent application. If tank mixing with tri-allate or trifluralin then follow label recommendations for those herbicides.
- Solubility is high and binding to organic matter is low, assisting rainfall to wash herbicide off the stubble.
- This also means the compound is freely available for root uptake and translocation once in the soil, however there is potential for leaching down the profile following large rainfall events. If applied to dry soil without mechanical incorporation, and followed by a significant rainfall event during emergence, there is the potential to move down the profile and damage germinating crops.
- Speed of breakdown depends on soil pH and moisture content. Plantback to sensitive crops can be very long in alkaline soils, especially under dry summer conditions. Observe label constraints for time and rainfall requirements.

### Triasulfuron

| Getting to the soil | | | When in the soil | | |
|---|---|---|---|---|---|
| Solubility (mg/L) | 815 | High | Binding ($K_{oc}$) | 60 | Mobile |
| Volatility (mPa) | 0.0021 | Non-volatile | Half-life ($DT_{50}$) | 16-92 (av. 39) | Non- persistent |
| Photodegradation | Insignificant | | Mobility | Highly solubility and low binding increases availability in the soil water | |
| Breakdown | Hydrolysis is the major breakdown pathway in neutral and low pH soils.<br>In alkaline soils, breakdown via hydrolysis is very slow and at high pH levels, slow microbial degradation becomes the primary route of dissipation. | | | | |

Practical considerations:

- With volatility and photodegradation both being low, the herbicide will not breakdown rapidly on the soil surface after application.
- Solubility is high and binding to organic matter is low, so will be readily washed off stubble following rainfall.
- This also means the herbicide is freely available for root uptake and translocation once in the soil, however there is potential for leaching down the profile following large rainfall events. If applied to dry soil without mechanical incorporation and followed by a significant rainfall event during emergence, there is the potential to move down the profile and damage germinating crops.
- Speed of breakdown depends on soil pH and moisture content. Plantback to sensitive crops can be very long in alkaline soils, especially under dry summer conditions. Observe label constraints for time and rainfall requirements.

## Imidazolinones

### Imazapic

| Getting to the soil | | | When in the soil | | |
|---|---|---|---|---|---|
| Solubility (mg/L) | 2 230 | High | Binding ($K_{oc}$) | 137 | Moderately mobile |
| Volatility (mPa) | 0.01 | Non-volatile | Half-life ($DT_{50}$) | 31-410 (av. 232) | Persistent |
| Photodegradation | Negligible | | Mobility | Moderate due to high solubility and only moderate binding | |
| Breakdown | Predominantly microbial. | | | | |

Practical considerations:

- With volatility and photodegradation both being low, the herbicide will not breakdown rapidly on the soil surface after application.
- High solubility and only moderate binding allows for the herbicide to be readily washed off stubble and incorporated with rainfall.
- Moderate binding prevents excessive losses via leaching. Binding increases at lower soil pH.
- Very persistent due to slow microbial breakdown, especially under conditions of low soil pH and low soil moisture. Substantial plantback constraints exist. Observe label constraints for pH, time and rainfall requirements.

### Imazethapyr

| Getting to the soil | | | When in the soil | | |
|---|---|---|---|---|---|
| Solubility (mg/L) | 1 400 | High | Binding ($K_{oc}$) | 52 | Mobile |
| Volatility (mPa) | 1.3 x $10^{-2}$ | Non-volatile | Half-life ($DT_{50}$) | 14-290 (av. 51) | Moderately persistent |
| Photodegradation | Negligible | | Mobility | Mobile in the soil water | |
| Breakdown | Predominantly microbial. | | | | |

Practical considerations:

- With volatility and photodegradation both being low, the herbicide will not breakdown rapidly on the soil surface after application.
- Imazethapyr has post-emergent and pre-emergent activity. Once in the plant it is readily translocated.
- Low binding in neutral and alkaline soils means the herbicide is likely to be freely available in soil water in many soils. Binding increases in soils with higher organic matter and soils where pH is below 6.5.
- Persistence is moderate, however it can be quite long under conditions of low soil pH and low soil moisture, where binding increases and microbial activity is reduced. Substantial plantback constraints to susceptible crops exist. Observe label constraints for pH, time and rainfall requirements.
- Crop selectivity comes from rapid metabolism in tolerant plants.

## Triazolopyrimidines

### Flumetsulam

| Getting to the soil | | | When in the soil | | |
|---|---|---|---|---|---|
| Solubility (mg/L) | 5 650 | High | Binding ($K_{oc}$) | 28 | Mobile |
| Volatility (mPa) | 3.7 x $10^{-7}$ | Non-volatile | Half-life ($DT_{50}$) | 45 | Moderately persistent |
| Photodegradation | Negligible | | Mobility | Mobile in the soil water | |
| Breakdown | Predominantly microbial. | | | | |

Practical considerations:

- Flumetsulam is primary used for post-emergent application in Australia, however in other countries it is primarily used as a pre-emergent herbicide.
- High solubility; easily taken up by roots and translocated within the plant.
- Crop selectivity comes from rapid metabolism in tolerant plants.
- Moderate persistence leads to plantback constraints (see label for details). Application rate will affect length of crop rotation restrictions in some situations. Breakdown will be fastest in soils with good microbial activity i.e. warm, moist soils.

# GROUP C

**Mode of action:** Group C herbicides work by inhibiting photosynthesis by binding at the photosystem II complex.

There are many sub-classes of Group C mode of action. The sub-classes of primary importance for pre-emergent use in Australian broadacre agriculture include:

- Triazines (e.g. atrazine, prometryn, simazine, terbuthylazine)
- Triazinones (e.g. metribuzin), and
- Ureas (e.g. diuron, fluometuron).

Group C resistant wild radish, ryegrass, barnyard grass, Indian hedge mustard and liverseed grass have been identified in Australia, however, as of 2017 they are typically infrequent and the extent of the spread of resistant populations has not developed as fast as it has to other modes of action.

**General properties:** Many Group C herbicides can be taken up by the plant either by root or foliar uptake however some (e.g. simazine) are primarily root uptake only.

Solubility of the triazines and ureas is typically low; therefore, very good soil moisture is usually required for effective root uptake from pre-emergent applications. When traizines and ureas are applied as a post-emergent foliar application, there is little movement outside of the treated leaf. Additional herbicide reaching the soil following a post-emergent application may be taken up by roots and transported within the xylem.

The triazinone herbicide metribuzin has high solubility so therefore is more easily taken up by plant roots and through foliage and is readily translocated.

Microbial breakdown occurs across the sub-classes of Group C chemistry; however, this is typically slow, especially under cool or dry conditions that do not encourage microbial populations.

For the triazine group, breakdown via hydrolysis also occurs. This breakdown path is much faster than microbial degradation and becomes the primary pathway on acidic and neutral soils. As soil pH increases, hydrolysis slows or stops, which then leaves slow microbial degradation as the primary method of breakdown. This leads to increased persistence of triazines on alkaline soils.

Where there has been long term, repeated use of triazine herbicides, and especially in situations where there is good soil organic matter, a process of 'enhanced microbial breakdown' can occur. Enhanced microbial breakdown occurs where there is a build-up of soil microflora with an enhanced capability to detoxify the herbicide. While this is more common in parts of the world with higher levels of soil organic matter than is typical in Australia, enhanced microbial degradation of triazines has been reported from multiple locations in Australia.

Differential selectivity between species is due to rapid detoxification. For example, some crops such as sorghum and maize are able to rapidly metabolise some triazine herbicides.

## Triazines

### Atrazine

| Getting to the soil | | | When in the soil | | |
|---|---|---|---|---|---|
| Solubility (mg/L) | 35 | Low | Binding ($K_{oc}$) | 89-513 (av. 100) | Moderately mobile |
| Volatility (mPa) | 0.039 | Non-volatile | Half-life ($DT_{50}$) | 6-108 (av. 60[@1]) | Moderately persistent |
| Photodegradation | Can be moderate, especially where not incorporated by rainfall | | Mobility | Can leach under high rainfall due to only moderate binding | |
| Breakdown | Microbial degradation is significant but typically slow. Under repeated applications microbial degradation has been shown to be accelerated. Hydrolysis is the primary breakdown pathway at soil pH below 6.5, however is slow at soil pH above 7.5 | | | | |

[@1] USDA Natural Resources Conservation Service.

Practical considerations:

- Unlikely to be lost via volatilisation after application. Losses to photodegradation can occur if not incorporated, especially if conditions remain dry after application.
- Low solubility means that substantial rainfall will be required to move herbicide off stubble and into the soil. Adequate rainfall will be required to wet the top 5cm of soil to incorporate the herbicide. If rainfall or irrigation is not expected then mechanical incorporation should be considered within a few days following application.
- Low solubility means that on-going good soil moisture is required for uptake by plant roots. Under dry conditions weed control is likely to be reduced.
- Soil binding is moderate however, it can be weak, especially on sandy soils, soils with low organic matter or alkaline soils. This can lead to herbicide moving down the profile with substantial rainfall events and may move to below the root zone of the weeds.
- Moderately persistent, with persistence increasing under conditions of high soil pH and low soil moisture. Application rates are typically high, so substantial plantback constraints are likely to exist for sensitive crops.
- Enhanced microbial degradation has been shown to occur where regular herbicide application occurs on the same soil.
- Has both root and shoot uptake, however translocation only occurs in an upward direction.

### Simazine

| Getting to the soil | | | When in the soil | | |
|---|---|---|---|---|---|
| Solubility (mg/L) | 5 | Low | Binding ($K_{oc}$) | 130 | Moderately mobile |
| Volatility (mPa) | 0.00081 | Non-volatile | Half-life ($DT_{50}$) | 27-102 (av. 90) | Moderately persistent |
| Photodegradation | Can degrade, especially if conditions are dry after application | | Mobility | Moderate binding reduces availability, however can be mobile in sandy or low organic matter soils | |
| Breakdown | Slow microbial degradation is the primary pathway in high pH soils. In neutral to acid soils, breakdown by non-microbial hydrolysis is more rapid than microbial breakdown. | | | | |

Practical considerations:

- Very low solubility and the possibility of photodegradation requires good rainfall after application to achieve suitable incorporation. Good soil moisture for the weeks after application is required for good weed control.
- Less binding in sandy or low organic matter soils may lead to more availability of the herbicide, increasing the risk of crop injury in susceptible crops grown on these soils.
- Persistence leads to plantback constraints, particularly in alkaline soils where the speed of hydrolysis is substantially reduced.
- Uptake is primarily via the roots, with negligible foliar uptake.

### Terbuthylazine

| Getting to the soil | | | When in the soil | | |
|---|---|---|---|---|---|
| Solubility (mg/L) | 7 | Low | Binding ($K_{oc}$) | 230[@1] | Moderately mobile |
| Volatility (mPa) | 0.152 | Non-volatile | Half-life ($DT_{50}$) | 6-149 (av. 22) | Non-persistent |
| Photodegradation | Limited, although may occur where not incorporated by rainfall | | Mobility | Moderate binding and low solubility reduces mobility and leaching | |
| Breakdown | Hydrolysis is the primary pathway in acidic soils. Slow microbial degradation is the primary pathway in alkaline soils. | | | | |

[@1] USDA Natural Resources Conservation Service.

Practical considerations:

- Unlikely to be lost via volatilisation after application unless soil remains dry for a number of weeks. Can be subject to photodegradation when applied to warm, dry soils without incorporation.
- Very low solubility means that substantial rainfall (20-30mm) will be required to move herbicide off stubble and into the soil to incorporate the herbicide.
- Very low solubility means that good soil moisture is required to permit uptake by plant roots. Under dry conditions weed control is likely to be reduced.
- Soil binding is stronger than atrazine and solubility lower, which is likely to keep the product closer to the soil surface and less likely to leach down the profile. However, if heavy rainfall occurs on lighter/sandy soils, then herbicide could still move into the root zone of germinating crops and crop damage may result. Stronger soil binding means that terbuthylazine may provide more consistent control of shallow or surface germinating weeds compared to atrazine and may also provide additional safety for deeper sown crops.
- The soil persistence of terbuthylazine is typically less than for some other triazines, however can be greatly extended on some soil types. Where dry conditions are experienced following application, plantbacks may need to be extended.

## Triazinones

### Metribuzin

| Getting to the soil | | | When in the soil | | |
|---|---|---|---|---|---|
| Solubility (mg/L) | 1100[#] | High | Binding ($K_{oc}$) | 60[#] | Mobile |
| Volatility (mPa) | 0.121 | Non-volatile | Half-life ($DT_{50}$) | 14-28[#] (av. 19) | Non- persistent |
| Photodegradation | Insignificant | | Mobility | Binds tighter to organic matter than soil. Binding decreases in alkaline soils. | |
| Breakdown | Microbial breakdown in the soil is the primary pathway | | | | |

[#] Shaner, D. (2014). Herbicide Handbook (10th Edition) Weed Society of America

Practical considerations:

- Unlikely to be significantly lost via volatilisation or photodegradation after application before suitable incorporation by rainfall.
- High solubility and low binding allows metribuzin to be mobile in the soil water phase.
- Availability in the soil is influenced by soil type, pH, organic matter and climate. Metribuzin will be most available (for both plant uptake and leaching) in sandy soils, alkaline soils and low organic matter soils. Label constraints may limit application in these situations and/or recommend lower application rates, so as to minimise crop injury from pre-emergent applications.
- Breakdown is typically relatively fast, however will be slowest in cool, dry conditions. Relatively short persistence does not normally influence the choice of crop the following year after application.

## Ureas

### Diuron

| Getting to the soil | | | When in the soil | | |
|---|---|---|---|---|---|
| Solubility (mg/L) | 36 | Low | Binding ($K_{oc}$) | 238-1 750 (av. 680) | Slightly mobile |
| Volatility (mPa) | $1.15 \times 10^{-3}$ | Non-volatile | Half-life ($DT_{50}$) | 90[#] | Moderately persistent |
| Photodegradation | Limited, although may occur where not incorporated by rainfall | | Mobility | Significant binding and low solubility reduces mobility and leaching in clay/high OM soils | |
| Breakdown | Microbial degradation is the primary breakdown pathway. Hydrolysis is insignificant. | | | | |

[#] Shaner, D. (2014). Herbicide Handbook (10th Edition) Weed Society of America

Practical considerations:

- Unlikely to be lost via volatilisation after application unless soil remains dry for a number of weeks, however some photodegradation may occur in this situation.
- Low solubility means that substantial rainfall will be required to move herbicide into the soil and adequate rainfall will be required to wet the top 5cm of soil to incorporate the herbicide.
- Relatively tight binding to organic matter may tie up a significant portion of applied herbicide under high stubble loads.
- Low solubility means that good soil moisture is required to permit uptake by plant roots. Under dry conditions, weed control is likely to be reduced.
- Primarily taken up by root absorption. Foliar uptake is less significant.
- Soil binding varies with soil type, in particular in relation to the clay and organic matter levels of the soil. In low clay / low organic matter soils, diuron may be loosely bound and hence subject to movement down the profile with heavy rainfall, with increased potential for crop injury.
- Soil persistence is relatively high and significant plantback requirements result.

## GROUP D

**Mode of action:** Group D herbicides bind to the major microtubule protein tubulin, which causes a loss of microtubule structure and inhibits mitosis. Often this can be observed as swelling/clubbing of the roots tips as cells cannot divide or elongate.

Within Group D, there are four sub-classes registered for use in Australia, however the primary classes used in broadacre agriculture are the dinitroanilines (DNA's) e.g. pendimethalin, trifluralin and the benzamides e.g. propyzamide.

Resistance to trifluralin is widespread in ryegrass throughout many states within Australia.

**General properties:** DNA herbicides characteristically have higher volatility, particularly on wet soils, and may also be subjected to photodegradation, particularly under warm conditions. Incorporation or soil coverage is recommended to minimise herbicide loss.

Use patterns developed in the 1970s & 1980s relied on full mechanical incorporation – often with multiple passes. However, recently, Australian use patterns have been developed enabling use of DNA herbicides in reduced and no-till farming.

For example, trifluralin can be applied immediately in front of the seeder, using this method to incorporate the herbicide and sow the crop in the one pass. The 'incorporate by sowing' technique (IBS) uses knife point seeders set up to throw soil into the inter-row to cover the herbicide and reduce volatilisation losses. This also removes treated soil from above the crop row, which increases crop selectivity, enabling higher rates than could have been used in the 'old' full incorporation use pattern. These higher application rates also provide some compensation for volatility losses from less than ideal incorporation and tie up on stubble. In no-till systems where most weed seed is on or near the soil surface, the levels of weed control achieved from a well-executed high rate IBS system, can be higher than that achieved in the older 'lower rate – full incorporation' system where weed seed and herbicide were diluted by mechanical mixing through the surface zone.

DNA herbicides typically have very low solubility and very strong binding to soil and organic matter. This can result in excessive 'tie up' on stubble or plant material present at application, which is then effectively lost as rainfall will be unable to wash it off the organic matter. The lipophilic nature, very low solubility and strong binding does not favour root uptake from herbicide available in the soil moisture. Primary entry into the germinating seedling comes via gaseous absorption through the roots and the coleoptile node or hypercotyl, as the seedling moves through the herbicide band.

Microbial degradation is the primary breakdown route.

### Crop selectivity and DNA herbicides

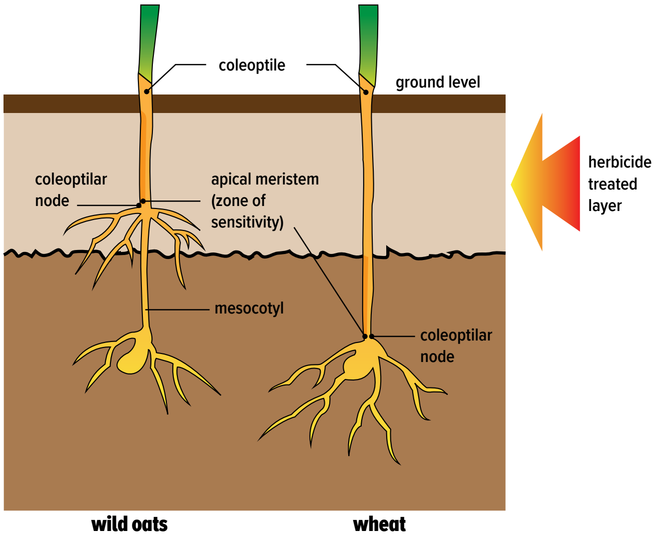
Herbicide selectivity comes from species tolerance (many broadleaf crops are more tolerant) and spatial separation of sensitive crop species (e.g. wheat, barley) from the herbicide. Spatial separation is achieved by using techniques such as sowing below the treated band and, with 'incorporate by sowing' applications, stripping away treated soil from above the sowing row.

For many grass weeds and cereal crops such as oats, maize and sorghum, the mesocotyl elongates during germination and this pushes the coleoptile node, from which the secondary roots grow, towards the surface (see Figure 10). In DNA susceptible species, having the secondary roots and the coleoptile node and mesocotyl (areas sensitive to DNA herbicide uptake) closer to the herbicide band increases availability for herbicide uptake by the germinating seeding.

In wheat and barley, the coleoptile node (and therefore primary and secondary root development) stays much closer to the seed, allowing for greater separation between the herbicide and the roots and coleoptile node that are sensitive to DNA herbicide uptake.

In zero till farming systems when using IBS application with knife points, the herbicide band is kept very close to the soil surface, maximising spatial separation of wheat and barley. This permits increased application rates to be used.

**Figure 10:** Different growth patterns in wild oats and wheat contribute to selectivity.



Source: Adapted from Hall (1999)

Where wheat or barley are to be sown following a pre-emergent DNA herbicide application, seeder set-up and operational speed needs to be carefully maintained and balanced with soil conditions and sowing boot design. Seeding equipment must provide adequate separation between the treated soil and cereal crop. Well set up equipment provides sufficient soil movement to cover the inter-row area to reduce volatility losses, while not throwing soil too far and into the furrow of the adjoining crop row. Tyned implements are far better at meeting these requirements than many low disturbance disc seeders, a requirement that is often reflected on product labels for the IBS technique. Press wheels help prevent treated soil from falling back into the furrow.

While DNA herbicides are tightly bound to the soil, should a significant rainfall event occur as the first incorporating rainfall, there is a risk that soil with bound herbicide can be washed into the sowing furrow and cause damage to the emerging cereal crop.

## Dinitroanilines

### Pendimethalin

| Getting to the soil | | | When in the soil | | |
|---|---|---|---|---|---|
| Solubility (mg/L) | 0.33 | Low | Binding ($K_{oc}$) | 10 241-36 604 (av. 17 491) | Non-mobile |
| Volatility (mPa) | 3.34 | Volatile | Half-life ($DT_{50}$) | 40-187 (av. 100) | Moderately persistent |
| Photodegradation | Can be subject to photodegradation if not incorporated | | Mobility | Binds tightly to soil and organic matter | |
| Breakdown | Microbial breakdown. | | | | |

Practical considerations:

- Can be subjected to losses from volatility and photodegradation. Follow label recommendations for incorporation instructions.
- Can be tied up on stubble or plant material present (e.g. weeds) during application.
- Once incorporated in the soil, pendimethalin will be bound tightly near the soil surface or where it has been placed, providing extended control.
- Rotational crop constraints apply. Follow label directions. Full cultivation to 15cm depth will assist in diluting residues through the soil profile.

### Trifluralin

| Getting to the soil | | | When in the soil | | |
|---|---|---|---|---|---|
| Solubility (mg/L) | 0.22 | Low | Binding ($K_{oc}$) | 15 880 | Non-mobile |
| Volatility (mPa) | 9.5 | Volatile | Half-life ($DT_{50}$) | 35-375 (av. 170) | Persistent |
| Photodegradation | Can be subject to photodegradation if not incorporated | | Mobility | Binds tightly to soil and organic matter | |
| Breakdown | Microbial breakdown. | | | | |

Practical considerations:

- Can be subjected to losses from volatility and photodegradation. Follow label recommendations for incorporation instructions.
- Can be tied up on stubble or plant material present (e.g. weeds) during application.
- Once incorporated in the soil, trifluralin will remain bound where it has been placed and provide extended control.
- Microbial degradation is slow, especially under cool, dry conditions. Rotational crop constraints apply. Follow label directions.
- When using cultivation for incorporation, avoid cereal varieties with short coleoptiles or seed treatments that shorten the coleoptile and ensure seeds are sown below the herbicide band.

## Benzamides

### Propyzamide

| Getting to the soil | | | When in the soil | | |
|---|---|---|---|---|---|
| Solubility (mg/L) | 9 | Low | Binding ($K_{oc}$) | 548-1 340 (av. 840) | Slightly mobile |
| Volatility (mPa) | 0.058 | Non-volatile | Half-life ($DT_{50}$) | 18-53[#] (av. 60[@7]) | Persistent |
| Photodegradation | Can be subject to photodegradation if not incorporated | | Mobility | Binds tightly to soil and organic matter | |
| Breakdown | Volatilisation and photodegradation can be significant without incorporation, especially under warm, dry conditions.<br>Microbial and non-microbial dissipation occur in the soil. | | | | |

[#] Shaner, D. (2014). Herbicide Handbook (10th Edition) Weed Society of America

[@7] Imtrade. (2017). Edge 900WG Safety Data Sheet

Practical considerations:

- Tie up on stubble will be significantly less than for trifluralin, with some of the propyzamide being able to be washed off the stubble and into the soil following adequate rainfall.
- Unlike the DNA's which are primarily taken up via gaseous diffusion into the roots and coleoptile node, propyzamide is primarily taken up by the roots from herbicide dissolved in the soil water. Low solubility means that good soil moisture is required for the period of weed control for herbicide uptake.
- Requires incorporation by sowing and rainfall (25mm) soon after application to reduce photodegradation and maximise herbicide performance.
- Relatively low solubility and significant binding will generally keep the herbicide near the soil surface. Weed seeds germinating close to the surface (as is usually the case in zero/minimal till farming), are likely to be well controlled, however weed seeds germinating from depth may keep their roots below treated soil.

# GROUP F

**Mode of action:** Group F herbicides cause inhibition of the phytoene desaturase enzyme (PDS inhibitors) within the chloroplasts. This prevents carotenoid synthesis which results in the characteristic bleaching effects typical of this mode of action.

Group F herbicides are typically effective via foliar application. However, some also demonstrate 'pre-emergent' activity when the shoots of germinating weeds take up the herbicide. Where control is achieved as a pre-emergent application, germinating weeds stop growing within days and may appear bleached before tissue necrosis, eventually leading to plant death.

The pyridazinone sub-class contains the horticultural herbicide norflurazon (not covered in this manual). The pyridinecarboxamide[3] sub-class contains picolinafen and diflufenican which can persist in the soil. Diflufenican may provide some limited activity on germinating weeds under certain conditions.

Resistance to this mode of action has been confirmed in Indian hedge mustard and wild radish.

**Diflufenican**

| Getting to the soil | | | When in the soil | | |
|---|---|---|---|---|---|
| Solubility (mg/L) | 0.05 | Low | Binding ($K_{oc}$) | 1622-2369$^{\#}$ | Slightly mobile |
| Volatility (mPa) | $4.25 \times 10^{-3}$ | Non-volatile | Half-life ($DT_{50}$) | 105-210# | Persistent |
| Photodegradation | Insignificant | | Mobility | Binds tightly to soil surface | |
| Breakdown | Metabolic degradation is slow. | | | | |

$^{\#}$ Shaner, D. (2014). Herbicide Handbook (10th Edition) Weed Society of America

Practical considerations:

- Tight binding and very low solubility sees the herbicide binding tightly to the soil surface.
- Rapid metabolism by cereals allows for crop selectivity when applied as a post-emergent application.
- Where registered, selectivity to legume and pulse crops comes from delaying application until seedlings are established and from sowing depth i.e. having roots established below the main herbicide band (see label for details). Some temporary crop effect may be observed from the over-the-top application, especially if the crop is under additional stress from other factors that may reduce the speed of metabolism.
- The low solubility means that translocation within the plant is minimal. For post-emergent application this means excellent spray coverage is required against small weeds. Tolerance increases rapidly with plant age.
- For pre-emergent activity, good soil moisture is required for consistent results. Pre-emergent weed control is achieved primarily by uptake via the shoot of the germinating weed moving through the treated soil. Weeds germinating from below the herbicide band on the soil surface may escape control.
- As the herbicide is tightly bound to the soil surface, thorough cultivation prior to sowing rotational crops is likely to dilute residues further by mixing soil through the profile.

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[3] Prior to 2014, CropLife Australia classified picolinafen in a picolinamide sub-class and diflufenican in a nicotinanilide sub-class. From 2014, these active ingredients have been combined into the pyridinecarboxamide sub-class of Group F.

# GROUP G

**Mode of action:** Group G herbicides inhibit protoporphyrinogen oxidase (commonly referred to as PPO or protox). The PPO enzyme is a required step in early-stage chlorophyll production and is responsible for converting protoporphyrinogen to protoporphyrin. Disrupting this reaction ultimately leads to lipid radicals which attack and oxidise lipids and proteins, resulting in a loss of chlorophyll and carotenoids and leaky cell membranes. This allows cells and cell organelles to dry out and disintegrate.

There are six different sub-classes of PPO available in Australia.

- Diphenylethers contain the broadacre herbicides acifluorfen (e.g. Blazer®) and oxyflurofen (e.g. Goal®)
- N-phenylphthalimides e.g. flumioxazin (Valor®, Terrain®)
- Oxadiazoles e.g. horticultural herbicides oxadiargyl and oxadiazon
- Phenylpyrazoles e.g. pyraflufen (Ecopar®)
- Pyrimidindiones contain the herbicides butafenacil (in Logran® B-Power®) and saflufenacil (Sharpen®) and
- Triazolinones e.g. carfentrazone (Affinity®).

Despite many years of commercial use in Australia, no resistance has been reported to date. This may be partially due to these herbicides most commonly being used as a secondary herbicide in a tank-mix with another mode of action. Internationally, resistance has been reported in both grass and broadleaf weeds, particularly from frequent use in soybean crops.

Most PPO inhibitors have little soil activity, however for some herbicides residual activity can be achieved at high application rates.

## Diphenylethers

### Oxyfluorfen

| Getting to the soil | | | When in the soil | | |
|---|---|---|---|---|---|
| Solubility (mg/L) | 0.1 | Low | Binding ($K_{oc}$) | >2 800[#] | Non-mobile |
| Volatility (mPa) | 0.026 | Non-volatile | Half-life ($DT_{50}$) | 31-172 (av. 73) | Moderately persistent |
| Photodegradation | May contribute to dissipation from dry soils if not incorporated. | | Mobility | Immobile in most soils (slightly mobile on extremely sandy soils) | |
| Breakdown | Moderately persistent. Microbial degradation is slow. | | | | |

[#] Shaner, D. (2014). Herbicide Handbook (10th Edition) Weed Society of America

Practical considerations:

- Oxyfluorfen is primarily used in broadacre cropping at very low application rates (up to 18gai/ha) as a tank mix added to knockdown herbicides. This use pattern provides very little residual activity, however it increases the speed of visual symptoms on weeds present at application and increases efficacy on certain specific weeds. To achieve medium term residual control, oxyfluorfen is registered for use in some horticultural crops at rates of 1kg ai/ha or higher.
- Oxyfluorfen is primarily active against many broadleaf weeds. Some grasses are controlled, particularly at the higher rates used in horticulture for residual control.

## N-phenylphthalimides

### Flumioxazin

| Getting to the soil | | | When in the soil | | |
|---|---|---|---|---|---|
| Solubility (mg/L) | 0.8 | Low | Binding ($K_{oc}$) | 889 | Slightly mobile |
| Volatility (mPa) | 0.32 | Non-volatile | Half-life ($DT_{50}$) | 16-20 (av. 18) | Non-persistent |
| Photodegradation | Stable on the soil surface. | | Mobility | Limited mobility in the soil. | |
| Breakdown | Primarily via microbial degradation. | | | | |

Practical considerations:

- Since introduction in Australia, flumioxazin use in broadacre situations has been via low rate knockdown applications, mixed with a knockdown herbicide, targeting increased speed of control of a range of broadleaf weeds. Under this use pattern, many rotational crops (excluding canola) can be planted immediately after application.
- When applied as a residual herbicide, the useful level of soil binding combined with low solubility will see flumioxazin remain relatively stable in the topsoil following incorporation.
- Recent registration of Terrain® has added residual control of a range of broadleaf weeds when applied prior to planting of wheat (excluding durum), faba beans, field peas and chickpeas. To achieve the desired period of weed free early crop protection, registered application rates for residual control at planting are increased six-fold compare to knockdown rates and increased rotational crop plantback periods apply.
- The very low solubility will mean that good soil moisture will be required to achieve adequate root uptake.

# GROUP H

**Mode of action:** Group H herbicides inhibit the enzyme 4-hydroxyphenylpyruvate dioxygenase (HPPD). Inhibiting HPPD ultimately prevents the formation of carotenoids, that protect chlorophyll in plants from being destroyed by sunlight. Plants appear bleached before plant death.

There are three main sub-classes of HPPD inhibitors used in Australia.

- Pyrazoles include the cereal post-emergent herbicide pyrasulfotole and the rice herbicide benzofenap
- Triketones which include the post-emergent herbicide bicyclopyrone and
- Isoxazoles e.g. isoxaflutole.

Group H chemistry was first commercialised in the early 1980s. To date, no herbicide resistance has been detected in Australia, however resistance has been confirmed in the USA.

## Pyrazoles

### Pyrasulfotole

| Getting to the soil | | | When in the soil | | |
|---|---|---|---|---|---|
| Solubility (mg/L) | 69 100 | High | Binding ($K_{oc}$) | 26-715 (av. 368) | Moderately mobile |
| Volatility (mPa) | 2.7 x $10^{-4}$ | Non-volatile | Half-life ($DT_{50}$) | 16-87 (av. 55) | Moderately persistent |
| Photodegradation | Stable on the soil surface. | | Mobility | Likely to be mobile in some soils | |
| Breakdown | Primarily microbial degradation. Dry conditions may extend re-cropping intervals. | | | | |

Practical considerations:

- The properties of pyrasulfotole allow it to be used as a foliar post-emergent application with little observed activity as a pre-emergent herbicide. However, soil persistence does occur and rotational crop constraints do exist.
- Pyrasulfotole is very soluble. Soil binding is variable, largely depending upon pH. These factors are likely to see pyrasulfotole mobile in the soil water in some soils.
- Breakdown is influenced by application rate, rainfall and soil pH (faster on acidic soils). Extended dry conditions may increase plantback periods.

## Triketones

### Bicyclopyrone

| Getting to the soil | | | When in the soil | | |
|---|---|---|---|---|---|
| Solubility (mg/L) | 119[@10] | Moderate | Binding ($K_{oc}$) | 6-50[@10] | Very mobile |
| Volatility (mPa) | <5 x $10^{-3}$[@10] | Non-volatile | Half-life ($DT_{50}$) | 2-36[@10] | Non- persistent |
| Photodegradation | Appears significant. | | Mobility | Likely to be mobile in most soils | |
| Breakdown | Photolysis appears significant under field conditions. Degrades quicker in acidic environments. | | | | |

[@10] APVMA. (2017). Evaluation of the new active bicyclopyrone in the product Talinor Herbicide

Practical considerations:

- Bicyclopyrone has been introduced into the Australian market as Talinor®, a co-formulation with bromoxynil, marketed as a post-emergent foliar uptake herbicide. The combination of Group H and Group C maximises the synergy that exists between these modes of action.
- With the use rates employed with Talinor, and the relatively short half-life, residual control will be limited, but some plantback constraints may exist.

## Isoxazoles

### Isoxaflutole

| Getting to the soil | | | When in the soil | | |
|---|---|---|---|---|---|
| Solubility (mg/L) | 6.2 | Low | Binding ($K_{oc}$) | 124-160 (av. 145) | Moderately mobile |
| Volatility (mPa) | $3.2 \times 10^{-5}$ | Non-volatile | Half-life ($DT_{50}$) | <2[@11] | See below |
| Photodegradation | Stable on the soil surface. Rainfall required to incorporate into the soil | | Mobility | Potential to be mobile in the soil on sandy or gravel soils | |
| Breakdown | Chemical hydrolysis and microbial degradation.<br>Breakdown is faster under warmer temperatures and higher pH! | | | | |

[@11] Bayer CropScience. (2011).

Practical considerations:

- After application, isoxaflutole remains stable on the soil surface. Isoxaflutole has very low solubility, however following rainfall, some herbicide will dissolve and go into solution. In soil solution, isoxaflutole has a very short half-life of less than 2 days, being broken down to diketonitrile (DKN) which is the herbicidal active compound. DKN has a $DT_{50}$ of 8-30 days.
- The extended residual control comes from more herbicide dissolving off the solid isoxaflutole after each rainfall event.
- DKN in the soil is broken down by microbial activity. Breakdown occurs faster under higher temperatures and higher soil pH.
- Crop selectivity in chickpeas results from a combination of sowing depth to provide adequate spatial separation between the herbicide and the root zone, and species tolerance that allows for rapid detoxification of the DKN. Some chickpea varieties, such as Yorker$^{(\phi)}$, are more susceptible and hence application is not recommended on this variety.
- Binding to soil and organic matter is moderate and solubility is very low, so movement down the profile is not common. However, in situations where a large rainfall event occurs following a dry period, it is possible to see herbicide residues move further down the profile and potentially into the root zone which may affect the crop, especially on sandy or gravel soils.
- Rotational constraints exist for some situations (refer to label). In addition to time, there is also a rainfall requirement as extended dry periods do not support isoxaflutole breakdown.

# GROUP I

**Mode of action:** Group I contains the synthetic auxin herbicides. When introduced into the plant they cause uncontrolled and abnormal cell division and growth, leading to cell destruction; or may inhibit cell division, particularly in the meristematic regions of the plant. Typical symptoms include twisting of new growth, before plant necrosis.

There are five sub-classes of Group I herbicides registered in Australia:

- Phenoxy carboxylic acids (e.g. 2,4-D, MCPA)
- Benzoic acids (e.g. dicamba)
- Pyridine carboxylic acids (e.g. aminopyralid, clopyralid, fluroxypyr, triclopyr, picloram), and
- Quinoline carboxylic acids (e.g. quinclorac)
- Arylpicolinates (e.g. halauxifen).

Dicamba has very short soil persistence and therefore does not provide effective residual control.  Quinclorac is only registered for use in turf.

Phenoxy and arylpicolinates have short persistence and may have short plantback constraints (usually measured in days to weeks), however they generally do not have any significant pre-emergent activity in grain crops at registered use rates. Pyridine carboxylic acids may provide residual activity.

Despite widespread use in Australia since the 1960s, resistance to this mode of action has been limited until relatively recently. Confirmed resistance exists in the phenoxy sub-class in wild radish (1999), Indian hedge mustard (2005), capeweed (2015) and, to multiple Group I sub-classes, in sowthistle (2015). The number of wild radish populations with resistance to Group I and resistance to other multiple modes of action is increasing rapidly, and poses a significant and major weed threat to crop production.

**General properties of the pyridine carboxylic acids:** The pyridine herbicides are typically suited to foliar uptake as the primary pathway into the plant. However most compounds have high solubility and relatively low binding providing potential for root uptake.

Persistence is typically moderate for many of the pyridines. However rotational crop constraints can be significant, especially at higher application rates and under conditions that do not favour microbial breakdown. Warm, moist conditions provide for fastest breakdown. For mobile compounds, leaching can also be significant.

The main exceptions from this group are fluroxypyr and halauxifen. Fluroxypyr, in the fluroxypyr-meptyl form, has very low solubility and tight binding. Small amounts of unbound herbicide convert to fluroxypyr acid which is more persistent. However, insufficient concentration of the acid is present to provide soil uptake in most situations, meaning minimal rotational crop constraints apply. Halauxifen has extremely short soil persistence, so is only effective as a foliar applied herbicide.

## Pyridine carboxylic acids

### Clopyralid acid

| Getting to the soil | | | When in the soil | | |
|---|---|---|---|---|---|
| Solubility (mg/L) | 7 850 | High | Binding ($K_{oc}$) | 3-7 (av. 5) | Very mobile |
| Volatility (mPa) | 1.36 | Volatile | Half-life ($DT_{50}$) | 2-14 (av. 18) [EU studies]<br>12-70 (av. 40) [US studies][#] | Moderately persistent |
| Photodegradation | Negligible | | Mobility | Potential to move with soil water | |
| Breakdown | Microbial breakdown is significant | | | | |

[#] Shaner, D. (2014). Herbicide Handbook (10th Edition) Weed Society of America

Practical considerations:

- Very high solubility and very low binding allows the compound to be freely available in the soil water phase, however there is increased binding over time.
- High bioavailability (potential to move with soil moisture) and low-level volatility is likely to make soil activity unreliable.
- Persistence can be moderate, especially in situations that do not favour microbial degradation (i.e. dry summers). Crop rotation restrictions can occur, especially after higher application rates. Follow label details for plantback considerations.

### Fluroxypyr-meptyl

| Getting to the soil | | | When in the soil | | |
|---|---|---|---|---|---|
| Solubility (mg/L) | 0.136 | Low | Binding ($K_{oc}$) | 19 550<br>39-71[#] for fluroxypyr acid. | Non-mobile |
| Volatility (mPa) | 0.01 | Non-volatile | Half-life ($DT_{50}$) | 3<br>34-68 (av. 51)<br>for fluroxypyr acid. | Non-persistent |
| Photodegradation | Not significant | | Mobility | Breaks down rapidly to fluroxypyr acid, which is more mobile. | |
| Breakdown | Relatively fast microbial degradation | | | | |

Practical considerations:

- Fluroxypyr is included here to highlight that it is very different to the other pyridine herbicides in its applied form.
- Fluroxypyr-mepthyl reaching the soil has very low solubility and tight binding. Available unbound herbicide in the soil water rapidly converts to the acid form, which is significantly more mobile and more persistent. Soil uptake of fluroxypyr is minimal in most situations.

### Picloram acid

| Getting to the soil | | | When in the soil | | |
|---|---|---|---|---|---|
| Solubility (mg/L) | 560 | High | Binding ($K_{oc}$) | 13 | Very mobile |
| Volatility (mPa) | $8 \times 10^{-5}$ | Non-volatile | Half-life ($DT_{50}$) | 20-49 (av. 36) [EU studies]<br>20-300 (av. 90)[#]<br>[US studies] | Moderately persistent |
| Photodegradation | Can be significant if applied to dry soil surface | | Mobility | Potential to leach, especially is sandy or low organic matter soils | |
| Breakdown | Photolysis and leaching can be significant pathways for loss.<br>Slow microbial degradation. Fastest under warm moist conditions. | | | | |

[#] Shaner, D. (2014). Herbicide Handbook (10th Edition) Weed Society of America

Practical considerations:

- Picloram is an effective herbicide when applied via foliar application, however can also be a useful pre-emergent herbicide on some weeds.
- Photodegradation can occur if applications are made to dry soil and incorporation by rainfall or cultivation does not occur for a number of weeks.
- High solubility and low binding allows easy incorporation by rainfall; however this also means that picloram is freely available in the soil water. There is potential to leach below the root zone in high rainfall situations, especially on sandy, low organic matter soils. Heavier soils with higher clay content and soils with higher organic matter will show some increase in binding.
- Persistence is typically moderate to long, however in situations where the climate is cool and dry, persistence can be substantially increased, particularly at higher application rates.

# GROUP J

**Mode of action:** Herbicides with the Group J mode of action inhibit fat synthesis within the plant. This affects waxy cuticle formation which is important in preventing water loss from the cells. Cell elongation and division are also affected.

There are four sub-classes of Group J herbicides registered in Australia, however only the thiocarbamate sub-class (e.g. prosulfocarb, tri-allate) are used in Australian grains production.

At present there is only very low incidence of resistance to the Group J mode of action in Australia.

**General properties:** When in the soil, these compounds are likely to bind tightly to the soil surface and not move down the profile. Without mechanical incorporation, the herbicide is likely to stay very close to the soil surface, so weeds germinating from depth may not be well controlled.

For prosulfocarb, root uptake is the primary entry pathway, with some foliar uptake possible on newly emerged seedlings. The primary entry route for tri-allate is vapor transfer into the coleoptile and coleoptile node, with some root uptake also occurring.

The low solubility of these compounds and their lipophilic properties limit translocation within the plant. For root uptake, very good soil moisture is required.

**Prosulfocarb**

| Getting to the soil | | | When in the soil | | |
|---|---|---|---|---|---|
| Solubility (mg/L) | 13.2 | Low | Binding ($K_{oc}$) | 1367-2340[#] | Slightly mobile |
| Volatility (mPa) | 0.79 | Non-volatile | Half-life ($DT_{50}$) | 7-13 (av. 10) | Non-persistent |
| Photodegradation | Insignificant | | Mobility | Tight binding and low solubility means herbicide will be bound at the soil surface. | |
| Breakdown | Rapid microbial breakdown is the primary pathway. | | | | |

[#] Shaner, D. (2014). Herbicide Handbook (10th Edition) Weed Society of America

Practical considerations:

- Prosulfocarb is available in Australia as a co-formulation with s-metolachlor (e.g. Boxer® Gold) and as straight prosulfocarb formulations (e.g. Arcade®).
- Prosulfocarb will bind moderately tightly to organic matter, leading to the possibility of tie up on stubble if there are high levels of organic matter present at application.
- The low solubility of prosulfocarb requires soils to be moist during the period of expected weed control for optimal results.
- Volatility and photodegradation are not major pathways for breakdown of prosulfocarb, however they are more significant for s-metolachlor. As a result, there is a label recommendation for Boxer® Gold (which contains both prosulfocarb and s-metolachlor) to be incorporated at sowing, or by rainfall, within 10 days of application.
- The short persistence of prosulfocarb requires high application rates to achieve the desired level of residual control.

**Tri-allate**

| Getting to the soil | | | When in the soil | | |
|---|---|---|---|---|---|
| Solubility (mg/L) | 4.1 | Low | Binding ($K_{oc}$) | 2 697-3 370 (av. 3 034) | Slightly mobile |
| Volatility (mPa) | 12 | Full mechanical incorporation required within 6 hours | Half-life ($DT_{50}$) | 8-205 (av.46) | Persistent |
| Photodegradation | Negligible | | Mobility | Significant binding and low solubility means herbicide will be bound at the soil surface. | |
| Breakdown | Loss due to volatility can be extremely high if not incorporated, especially in warm soils.<br>Once in the soil breakdown is via microbial degradation. | | | | |

Practical considerations:

- The majority of seedling uptake is via absorption into the coleoptile emerging through the treated soil.
- Tri-allate is one of the more volatile herbicides commonly used in the Australian grain industry. Herbicide labels recommend full mechanical incorporation into moist soil within 6 hours of application when used in a cultivation system. Two passes (e.g. cultivation or heavy harrows followed by full disturbance sowing) will provide better incorporation than a single pass. Incorporate tri-allate to a depth of 5 to 7cm.
- In a reduced tillage farming system using the knife point IBS technique for incorporation, label rates are increased (compared to rates used in a conventional tillage system) to counteract losses from volatilisation at application, increased binding to stubble and to achieve better ryegrass control.
- Low solubility means that good soil moisture is required for the period where weed control is required. Dry conditions post-application are likely to reduce weed control, especially if the soil dries out on the surface where the herbicide is bound, but is moist at depth where weeds are germinating.

# GROUP K

**Mode of action:** Group K herbicides inhibit very long chain fatty acid (VLCFA) synthesis. This prevents cell expansion in the germinating seedling.

There are two primary subclasses used in Australian grain crops:

- Chloroacetamides (e.g. dimethenamid-P, metazachlor, s-metolachlor), and
- Isoxazolines (e.g. pyroxasulfone).

At present, resistance to this mode of action in the field is limited, both within Australia and internationally, despite extensive use of this mode of action for over 40 years.

**General properties:** Group K herbicides are absorbed by the germinating seedling, affecting VLCFA synthesis and ultimately preventing seedling establishment. Typically, these herbicides are more effective against monocots at the application rates used in Australia, however some small seeded dicots may also be susceptible.

Selectivity when used in cereals comes from a combination of the ability of some species to rapidly detoxify the herbicide; application rate; manipulation of sowing depth to be below the herbicide band; and spatial separation at sowing by throwing treated soil away from the seeding furrow. For sorghum, the addition of Concep® II (oxabetrinil) to the seed enhances crop metabolism of s-metolachlor, thus increasing selectivity.

Herbicides with this mode of action tend to have low to moderate soil binding, especially in low organic matter or sandy soils. Heavy rainfall between application and crop emergence can lead to herbicide moving down the soil profile and affecting the crop. In particular, damage occurs where waterlogging impairs the crop's ability to metabolise and detoxify the herbicide.

## Chloroacetamides

### Dimethenamid-P

| Getting to the soil | | | When in the soil | | |
|---|---|---|---|---|---|
| Solubility (mg/L) | 1 499 | High | Binding ($K_{oc}$) | 40-474 (av. 218[@1]) | Moderate mobility |
| Volatility (mPa) | 2.5 | Volatile | Half-life ($DT_{50}$) | 2-16 (av. 7) | Non-persistent |
| Photodegradation | Little impact | | Mobility | Can be high, especially on lighter soils. | |
| Breakdown | Microbial degradation is the primary pathway. | | | | |

[@1] USDA Natural Resources Conservation Service.

Practical considerations:

- The vapour pressure of dimethenamid-P indicates that some product could be lost to the environment over time in hot, dry conditions if not incorporated. To address this and the relatively short persistence, the Australian label recommends incorporation by sowing using a knife point or narrow tyne system.
- High solubility and moderate binding on some soils indicates that dimethenamid-P could be incorporated with minimal rainfall, however it has the potential to be mobile in some soils with high rainfall.
- Low disturbance disc seeder systems are not recommended, as the herbicide needs to be removed from the sowing furrow. High solubility could lead to the herbicide moving down the sowing slot before binding occurs, if there is moderate to heavy rainfall after sowing.
- Relatively short persistence means that high application rates are required to achieve the desired length of pre-emergent weed control. Extended rotational crop limitations are unlikely except in specific crops in the following year, due to rapid breakdown. Check the product label for specific directions.

### Metazachlor

| Getting to the soil | | | When in the soil | | |
|---|---|---|---|---|---|
| Solubility (mg/L) | 450 | Moderate | Binding ($K_{oc}$) | 29-73 (av. 54) | Mobile |
| Volatility (mPa) | 0.093 | Non-volatile | Half-life ($DT_{50}$) | 3-21 (av. 7) | Non-persistent |
| Photodegradation | Not a major degradation route[@14] | | Mobility | Likely to be mobile in the soil water. | |
| Breakdown | Multi-step enzyme driven metabolism[@14]. | | | | |

[@14] APVMA. (2016). Evaluation of the new active metazachlor in the product Butisan

Practical considerations:

- Solubility is moderate and binding relatively low, so herbicide will be easily washed off stubble following minimal rainfall.
- Short persistence is unlikely to cause significant crop rotation restrictions the following season.
- Metazachlor will be mobile in the water phase in the soil, potentially moving down to the seeding zone and has potential to leach further down the profile.

### S-metolachlor

| Getting to the soil | | | When in the soil | | |
|---|---|---|---|---|---|
| Solubility (mg/L) | 480 | Moderate | Binding ($K_{oc}$) | 200[#] | Moderate mobility |
| Volatility (mPa) | 3.7 | Volatile | Half-life ($DT_{50}$) | 11-31 (av. 21) | Non-persistent |
| Photodegradation | Can be significant when applied to dry soils and not incorporated | | Mobility | Level of binding is influenced by organic matter and clay content. | |
| Breakdown | Losses from volatility are generally low; however, losses via photodegradation can be high if not incorporated. Microbial degradation is the primary route post incorporation. | | | | |

[#] Shaner, D. (2014). Herbicide Handbook (10th Edition) Weed Society of America

Practical considerations:

- Photodegradation and volatilisation loses can be significant if not incorporated (mechanical or rainfall) after application. Avoid applying under hot, dry conditions if no rainfall is forecast within the next 7 to 10 days and mechanical incorporation is not employed.
- The solubility of s-metolachlor implies that incorporation can be achieved without the need for large volumes of rainfall. If heavy rainfall or irrigation occurs as the first event after application, then s-metolachlor can be prone to leaching before the herbicide has bound to the soil, especially on sandy or low organic matter soils.
- Binding varies, depending upon soil type and organic matter. S-metolachlor binds more tightly to organic matter than clay and therefore can be subject to some level of tie up in situations of heavy stubble or weeds at application. In soils with higher clay content and/or organic matter, s-metolachlor tends to bind near the surface unless subjected to large rainfall events before binding has occurred.
- In soils with low clay content or organic matter, s-metolachlor will be loosely bound and hence can move down the profile out of the zone of surface germinating weeds. In these soils, there is also the potential for crop injury if herbicide is moved down to the germination zone of the crop, or can be lost through leaching.
- Persistence of s-metolachlor is relatively short. In Australian use patterns, cereal crops can be sown following a pre-emergent application when using low application rates. In summer crop situations, moderate length of residual control is achieved by applying significantly higher rates than used before sowing cereals.
- In sorghum, crop selectivity is improved by treating the seed with Concep® II seed safener. This leads to faster metabolism/detoxification of the herbicide by the crop.

## Isoxazolines

### Pyroxasulfone

| Getting to the soil | | | When in the soil | | |
|---|---|---|---|---|---|
| Solubility (mg/L) | 3.49 | Low | Binding ($K_{oc}$) | 119-226 (av. 223) | Moderate mobility |
| Volatility (mPa) | $2.4 \text{ x } 10^{-3}$ | Non-volatile | Half-life ($DT_{50}$) | 16-26 (av. 22) | Non-persistent |
| Photodegradation | Only minor degradation pathway[@15] | | Mobility | Relatively weak binding may allow movement down the profile | |
| Breakdown | Primarily microbial | | | | |

[@15] APVMA. (2011). Evaluation of the new active pyroxasulfone in the Product Sakura® 850 WG Herbicide

Practical considerations:

- Low solubility and moderate binding require significant rainfall to wash herbicide off stubble. However heavy rainfall after application in soils with low organic matter can see herbicide moved down the profile and into contact with the germinating wheat seed which can result in crop injury.
- Low solubility means that good ongoing soil moisture is required for uptake by the germinating weeds. Dry soil conditions between application and weed emergence can result in poor control.
- Incorporation by sowing coupled with rainfall after application is recommended to reduce off-target herbicide movement.

# PROPERTIES OF PRE-EMERGENT HERBICIDES USED IN AUSTRALIAN GRAIN PRODUCTION SYSTEMS

**The following table lists the important properties influencing soil availability for selected pre-emergent herbicides used in Australian broadacre farming systems. By understanding these properties and how they inter-relate, advisers will be better able to plan for, predict and interpret field outcomes.**

**Note:** An example of a common trade name is given to assist in identification of the active ingredient only. As noted in the table, some active ingredients are not commercially available in Australia as a single active formulation and contain at least one other active ingredient, so the properties of this additional active ingredient will also need consideration. The information in this table is for the active ingredient. In some situations it may be possible to alter these properties in the field by formulation design – for example an encapsulated formulation may reduce losses due to volatility.

**Table 7: Properties of selected herbicides used in Australian grains production.**

*(The basis of inclusion in this table are products that are used in broadacre systems that also have plantback constraints on their label – indicating a level of residual activity).*

Unless otherwise stated, values quoted specific to the active ingredients in the tables below have been sourced from the Pesticide Properties Database which can be found at http://sitem.herts.ac.uk/aeru/iupac/index.htm University of Hertfordshire. (2006-2019). The Pesticide Properties DataBase (PPDB) developed by the Agriculture & Environment Research Unit (AERU), University of Hertfordshire. Accessed on 2nd October 2019.

| Mode of action | | Active ingredient | Common trade name | Solubility[1] (mg/L @ 20°C) | Volatility[2] | Persistence[3] (DT50) | Mobility in the soil[4] (Koc) | Primary breakdown pathway[#] |
|---|---|---|---|---|---|---|---|---|
| A | Fop's | diclofop-methyl | various | 0.39<br>(low) | 2.5 x $10^{-2}$ | 7-39 (av. 19) | 16 000[#]<br>(non-mobile) | Hydrolysed to diclofop acid within a few days. |
| | | | diclofop acid | 122 700<br>(high) | 3.1 x $10^{-6}$ | 25-52 (av. 35) | | |
| | | fenoxaprop-P-ethyl | Foxtrot® | 0.43<br>(low) | 6.5 x $10^{-3}$ | 0.3 | 5 419-26 200 (av. 11 354)<br>(non-mobile) | Rapid hydrolysis to fenoxaprop acid. |
| | | | fenoxaprop-P acid | 61 000<br>(high) | 0.18 | 8 | | Microbial degradation. |
| | | fluazifop-P-butyl | Fusilade® | 0.93<br>(low) | 0.12 | 2-38 (av.8.2) | 3 394<br>(slightly mobile) | Hydrolysis to fluazifop acid. |
| | | | fluzaifop-P acid | 40.5<br>(low) | | 25 | 106-304 (av. 205)<br>(moderate) | Microbial degradation. |
| | | haloxyfop-P-methyl | Verdict® | 7.9<br>(low) | 0.055 | 0.5 | Methyl ester estimated to be non-mobile[#] | Rapid hydrolysis to haloxyfop acid. |
| | | | haloxyfop-P acid | 375<br>(moderate) | 4 x $10^{-3}$ | 13-36 (av. 17) | 42-114 (av. 66)<br>(mobile) | Microbial degradation. |
| | | propaquizafop | Shogun® | 0.63<br>(low) | 4.39 x $10^{-7}$ | 3[#] | 204-472[#]<br>(slightly mobile) | Microbial degradation.<br>Degrades rapidly to quizalofop. |
| | | quizalofop-P-ethyl | Targa® | 0.6<br>(low) | 1.1 x $10^{-4}$ | 0.6-8 (av. 1.8) | 510[#]<br>(slightly mobile) | Quizalofop acid is a primary metabolite. |
| | | | quizalofop-P acid | 1 000<br>(high) | | 31-39 (av. 35) | | Rapid microbial degradation. |
| | Dim's | butroxydim | Factor®<br>(low) | 6.9 | 0.001 | 9 | 635<br>(slightly mobile) | Rapid microbial degradation. |
| | | clethodim | Select® | 5 450<br>(high) | 2.08 x $10^{-3}$ | 3 | | Very rapid soil degradation.<br>Major metabolite is clethodim sulfoxide DT50 = 17 days. |
| | | tralkoxydim | Achieve® | 6.1<br>(low) | 3.7 x $10^{-4}$ | 1.9 | 35 - 314 (av. 120)<br>(moderate) | Rapid microbial degradation. |
| | Den's | pinoxaden | Axial® | 200<br>(moderate) | 2.0 x $10^{-4}$ | 0.6 | 299-852[#]<br>(av. 300)[@1]<br>(moderate) | Hydrolysis and microbial degradation. |

## Table 7: (contd.) Properties of selected herbicides used in Australian grains production.

*(The basis of inclusion in this table are products that are used in broadacre systems that also have plantback constraints on their label – indicating a level of residual activity).*

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| Mode of action | | Active | Common trade name | Solubility[1] (mg/L @ 20°C) | Volatility[2] | Persistence[3] (DT50) | Mobility in the soil[4] (Koc) | Primary breakdown pathway[#] |
|---|---|---|---|---|---|---|---|---|
| B | SU's | chlorsulfuron | various | 12 500<br>(high) | $3.07 \times 10^{-6}$ | 10-185 (av. 36) | 40[#]<br>(mobile) | Hydrolysis is the primary pathway in neutral and acidic soils. Slow microbial degradation and slow hydrolysis is the primary pathway in alkaline soils. |
| | | halosulfuron-methyl | Sempra® | 10<br>(low) | $3.5 \times 10^{-2}$ | 14 | 31-199 (av. 109)<br>(moderate) | Rapid hydrolysis and microbial degradation |
| | | iodosulfuron-methyl-sodium | Hussar® | 25 000<br>(high) | $2.6 \times 10^{-6}$ | 1-10 (av. 3) | 10 – 90[#]<br>(av. 45)[@1]<br>(mobile) | Rapid hydrolysis in neutral and acidic soils. Microbial breakdown becomes dominant in neutral to alkaline soils[@3]. Metsulfuron is a major metabolite. |
| | | mesosulfuron-methyl | Atlantis® | 483<br>(moderate) | $1.1 \times 10^{-5}$ | 46-76[@2] (av.78) | 26-354[@2] (av. 40)[@1]<br>(mobile) | Hydrolysis. However microbial degradation appears to be also significant at low temperatures[@1]. |
| | | metsulfuron-methyl | Ally® | 2 790<br>(high) | $1.4 \times 10^{-8}$ | 7-37 (av. 13) | 35[#]<br>(mobile) | Rapid hydrolysis at lower soil pH. Slow microbial degradation and hydrolysis on alkaline soils. |
| | | sulfosulfuron | Monza® | 1 627<br>(high) | $3.05 \times 10^{-5}$ | 29-75 (av. 45) | 47[@1]<br>(mobile) | Hydrolysis is the primary pathway in neutral and acidic soils. Slow microbial degradation and slow hydrolysis is the primary pathway in alkaline soils. |
| | | triasulfuron | Logran® | 815<br>(high) | 0.0021 | 16-92 (av. 39) | 60<br>(mobile) | Hydrolysis is the primary pathway in neutral and acidic soils. Slow microbial degradation is the primary pathway in alkaline soils. |
| | | tribenuron-methyl | Express® | 2 483<br>(high) | $5.99 \times 10^{-6}$ | 2-10 (av. 4) | 8-91 (av. 35)<br>(mobile) | Rapidly degraded by hydrolysis and microbes. |
| | IMI's | imazamox | Raptor® | 626 000<br>(high) | 0.0133 | 17 | 62[@1]<br>(mobile) | Rapid microbial degradation. Binding increases in acidic soils, increasing persistence. |
| | | imazapic | Flame® | 2 230<br>(high) | 0.01 | 31-410<br>(av. 232) | 137<br>(moderate) | Slow microbial degradation. Binding increases in acidic soils, increasing persistence. |
| | | imazapyr | Arsenal® | 9 740<br>(high) | 0.013 | 25-142[#]<br>(av. 90[@1]) | 100[@1]<br>(moderate) | Slow microbial degradation. Binding increases in soils with pH <6.5 which increases persistence. |
| | | imazethapyr | Spinnaker® | 1 400<br>(high) | $1.33 \times 10^{-2}$ | 7-290 (av. 51) | 52<br>(mobile) | Slow microbial degradation. Binding increases in soils with pH <6.5 which increases persistence. |
| | TP's | florasulam | Paradigm®[A] | 6 360<br>(high) | 0.01 | 2-18 (av. 8.5) | 22<br>(mobile) | Fast microbial degradation, especially under warm, moist conditions. |
| | | flumetsulam | Broadstrike® | 5 650<br>(high) | $3.70 \times 10^{-7}$ | 45 | 28<br>(mobile) | Microbial degradation is the primary pathway. This occurs faster at higher pH. |
| | | metosulam | Eclipse® | 7 00<br>(high) | $1 \times 10^{-9}$ | 20-47 (av. 39) | 166[@4]<br>(moderate) | Microbial.[@5] |
| | | pyroxsulam | Crusader® | 3 200<br>(high) | $1 \times 10^{-4}$ | 5-29[@6] (av. 13) | 8-54 (av. 33)<br>(mobile) | Rapid microbial degradation.[@6] |
| C | Triazines | atrazine | Gesaprim® | 35<br>(low) | 0.039 | 6-108 (av. 60[@1]) | 89-513 (av. 100)<br>(moderate) | Hydrolysis is the primary pathway in neutral and acidic soils. Slow microbial degradation is the primary pathway in alkaline soils. |
| | | cyanazine | Bladex® | 171<br>(moderate) | 0.000213 | 12-25 (av. 14)[#] | 190<br>(moderate) | Microbial degradation is the primary degradation pathway. Hydrolysis also occurs rapidly in acidic soils. |
| | | prometryn | Gesagard® | 33<br>(low) | 0.11 | 60[#] | 400<br>(moderate) | Microbial |

## Table 7: (contd.) Properties of selected herbicides used in Australian grains production.

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| Mode of action | | Active | Common trade name | Solubility[1] (mg/L @ 20°C) | Volatility[2] | Persistence[3] (DT50) | Mobility in the soil[4] (Koc) | Primary breakdown pathway[#] |
|---|---|---|---|---|---|---|---|---|
| C | Triazines | simazine | Gesatop® | 5<br>(low) | 0.00081 | 27-102 (av. 90) | 130<br>(moderate) | Hydrolysis is the primary pathway in neutral and acidic soils. Slow microbial degradation is the primary pathway in alkaline soils. |
| | | terbuthylazine | Terbyne® | 7<br>(low) | 0.152 | 16-149 (av. 22) | 230[@1]<br>(moderate) | Hydrolysis is the primary pathway in neutral and acidic soils. Slow microbial degradation is the primary pathway in alkaline soils. |
| | Triazinones | metribuzin | Sencor® | 1100[#]<br>(high) | 0.121 | 14-28[#] (av. 19)<br>30-60 under cool dry conditions[#] | 60[#]<br>(mobile) | Microbial. |
| | Urea's | diuron | diuron | 36<br>(low) | 1.15 x $10^{-3}$ | 90[#] | 238-1 750 (av. 680)<br>(slightly mobile) | Volatilisation and photodegradation losses are typically low, but can be significant under hot and dry conditions if not incorporated. Slow microbial degradation in the soil. |
| | | fluometuron | Cotoran® | 111<br>(moderate) | 0.125 | 63-117 (av. 90) | 100[#]<br>(moderate) | Photodegradation is significant, especially under dry conditions. Slow microbial metabolism in the soil. |
| D | DNA's | pendimethalin | Stomp® | 0.33<br>(low) | 3.34<br>(volatile) | 40-187 (av. 100) | 10 241-36 604<br>(av. 17 491)<br>(non-mobile) | Subject to photodegradation and volatility loss if not incorporated. Slow microbial degradation in the soil, rapid under waterlogged conditions. |
| | | trifluralin | Treflan® | 0.22<br>(low) | 9.5<br>(volatile) | 35-375 (av. 170) | 15 800<br>(non-mobile) | Subject to photodegradation and volatility loss if not incorporated. Slow microbial degradation in the soil, faster under waterlogged conditions. |
| | Benzamides | propyzamide | Rustler® | 9<br>(low) | 0.058 | 18-53[#] (av. 60[@7]) | 548-1 340 (av. 840)<br>(slightly mobile) | Volatilisation and photodegradation can be significant without incorporation, especially under warm, dry conditions. Microbial and non-microbial dissipation occur in the soil. |
| F | pyridinecarboxamide | diflufenican | Brodal® | 0.05<br>(low) | 4.25 x $10^{-3}$ | 105-210[#] | 1622-2369[#]<br>(non-mobile) | Binds tightly to soil. Metabolic degradation is slow. |
| | | picolinafen | Sniper® | 0.047<br>(low) | 1.7 x 10-4 | 9-64 (av. 31) | 28300<br>(non-mobile) | Mineralisation to CO$_2$ and two primary metabolites. |
| G | diphenylether | oxyfluorfen | Goal® | 0.1<br>(low) | 0.026 | 31-172 (av. 73) | >2 800[#]<br>(non-mobile) | Photolysis is important.<br>Microbial breakdown is slow. |
| | N-phenylphthalimide | flumioxazin | Valor® | 0.8<br>(low) | 0.32 | 16-20 (av. 18) | 889<br>(slightly mobile) | Microbial. |
| | Pyrimidindione | saflufenacil | Sharpen® | 2 100<br>(high) | 4.5 x $10^{-12}$ | 7-35 (av. 20) | 9-55[@8]<br>(mobile) | Primarily microbial. Photolysis can contribute under field conditions.[@8] |
| H | Pyrazole | pyrasulfotole | Precept®[B] | 69 100<br>(high) | 2.7 x $10^{-4}$ | 16-87 (av. 55) | 22-715 (av. 368)<br>(moderate) | Microbial.[@9] |
| | Triketone | bicyclopyrone | Talinor®[C] | 119[@10]<br>(moderate) | <5 x $10^{-3}$ [@10] | 2-36[@10] | 6-50[@10] in most soils<br>(very mobile) | Photolysis appears significant under field conditions.[@10] |

## Table 7: (contd.) Properties of selected herbicides used in Australian grains production.

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| Mode of action | | Active | Common trade name | Solubility[1] (mg/L @ 20°C) | Volatility[2] | Persistence[3] (DT50) | Mobility in the soil[4] (Koc) | Primary breakdown pathway[#] |
|---|---|---|---|---|---|---|---|---|
| H | Isoxazole | isoxaflutole | Balance® | 6.2<br>(low) | 3.22 x $10^{-5}$ | 0.5-2.4 (av. 1.3) | 124-160 (av. 145)<br>(moderate) | Rapid chemical hydrolysis to the active metabolite. |
| | | | diketonitrile metabolite | 22 660<br>(high) | 2.6 x $10^{-4}$ | 8-30[@11] (av. 9) | | Microbial degradation. |
| I | Arylpicolinate | halauxifen-methyl | Paradigm®[A] | 1.67[@12]<br>(low) | 1.5 x $10^{-5}$ | 1.5[@12] | 473-2 659 (av. 1 418)[@12]<br>(slightly mobile) | Rapid degradation to the acid then microbial degradation.[@12] Photodegradation is insignificant relative to microbial degradation. |
| | | | halauxifen acid | 3070<br>(high) | | 14[@12] | 34-539 (av. 173)<br>(moderate) | |
| | Benzoic acid | dicamba | Cadence® | 250 000<br>(high) | 1.67 | 3-5 (av. 3.9) | 2[#]<br>(very mobile) | Rapidly metabolised and lost to leaching.[#]<br>(very mobile) |
| | Phenoxys | 2,4-D dimethylamine | amine 625 | 729 000[#]<br>(high) | Rapidly dissociates to 2,4-D acid | | | |
| | | 2,4-D 2-ethylhexyl ester | LVE 680 | 0.086[#]<br>(low) | 0.49[#] | 9[@1] | 53[@1] | Undergoes hydrolysis to 2,4-D acid in the soil. |
| | | | 2,4-D acid | 569[#]<br>(high) | 0.009 | 22-38 (av. 29) | 23-275 (av. 39)<br>Absorption increases with higher OM and/or lower pH | Microbial. |
| | | MCPA dimethylamine | 750 amine | 866 000[#]<br>(high) | | 25[@1] | 20[#] | |
| | | MCPA 2-ethylhexyl ester | LVE 570 | 0.5[@1]<br>(low) | | 7[@1] | 136[@1] | |
| | | | MCPA acid | 825[@1]<br>(high) | 0.4 | 25 | 110[#]<br>(moderate) | Microbial degradation is the primary loss pathway. Some leaching and minor volatilisation. |
| | Pyridines | aminopyralid | Hotshot®[D] | 2 480<br>(high) | 2.59 x $10^{-9}$ | 8-35 (av. 21) | 11[#]<br>(very mobile) | Moderate potential for leaching. Primarily microbial degradation. |
| | | clopyralid acid | Lontrel® | 7 850<br>(high) | 1.36[#] | 2-14 (av. 8)<br>[EU studies]<br>12-70 (av. 40)<br>[US studies][#] | 3-7 (av. 5)<br>(very mobile) | Leaching can be significant. Microbial degradation, fastest in warm, moist soils. |
| | | fluroxypyr-meptyl | Starane® | 0.136<br>(low) | 0.01 | 3 | 19 550 | Rapidly converts to fluroxypyr acid in the soil. |
| | | | fluroxypyr acid | 6500<br>(high) | 3.8 x $10^{-6}$ | 34-68 (av. 51) | 39-71[#]<br>(mobile) | Microbial breakdown. |
| | | picloram acid | Tordon® | 560<br>(high) | 8.0 x $10^{-5}$ | 20-49 (av. 36)<br>[EU studies]<br>20-300 (av. 90)[#]<br>[US studies]<br>Increases with application rate. | 13<br>(very mobile) | Photolysis and leaching can be significant. Slow microbial degradation. Fastest under warm moist conditions. |
| | | triclopyr-butoxyethyl | Garlon® | 23[#]<br>(low) | | | 780[#]<br>(slightly mobile) | Rapidly converts to triclopyr acid in the soil. |
| | | | triclopyr acid | 435[#]<br>(moderate) | 1.6 x $10^{-4}$[#] | 10-46 (av. 30)[#] | 35[#]<br>(mobile) | Microbial breakdown. |
| J | thiocarbamates | prosulfocarb | Arcade® | 13.2<br>(low) | 0.79 | 7-13 (av. 10) | 1367-2340[#]<br>(non-mobile) | Microbial breakdown. |
| | | tri-allate | Avadex® | 4.1<br>(low) | 12 | 8-205 (av. 46) | 2 697-3 370 (av. 3 034)<br>(non-mobile) | Volatilisation and microbial. |

## Table 7: (contd.) Properties of selected herbicides used in Australian grains production.

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| Mode of action | | Active | Common trade name | Solubility[1] (mg/L @ 20°C) | Volatility[2] | Persistence[3] (DT50) | Mobility in the soil[4] (Koc) | Primary breakdown pathway[#] |
|---|---|---|---|---|---|---|---|---|
| K | chloroacetamides | dimethenamid-P | Outlook® | 1 499 (high) | 2.5 | 2-16 (av. 7) | 40-474[@13] (av. 218[@1]) (moderate) | Microbial. |
| | | metazachlor | Butisan® | 450 (moderate) | 0.093 | 3-21 (av. 7) | 29-73 (av. 54) (mobile) | Photolysis is not a major degradation route.[@14] Multi-step enzyme driven metabolism.[@14] |
| | | s-metolachlor | Dual® | 480 (moderate) | 3.7 | 11-31 (av. 21) | 200[#] (moderate) | Volatility generally low but photodegradation can be high prior to incorporation. Microbial degradation. |
| | Isoxazolines | pyroxasulfone | Sakura® | 3.49 (low) | 2.4 X $10^{-3}$ | 16-26 (av. 22) | 119-226 (av. 223) (moderate) | Microbial via cleavage of the methyl-sulfone bridge.[@15] |
| O | | isoxaben | Gallery® | 0.93 (low) | 5.5 x $10^{-4}$ | 66-309 (av. 123) | 700-1290 (av. 909) (slightly mobile) | Microbial. |

Unless otherwise stated, information in this table is sourced from the Pesticide Properties Database which can be found at http://sitem.herts.ac.uk/aeru/iupac/index.htm University of Hertfordshire. (2006-2019). The Pesticide Properties DataBase (PPDB) developed by the Agriculture & Environment Research Unit (AERU), University of Hertfordshire, 2006-2017. Accessed on 2nd October 2019.

[1] Solubility in water (mg/L @ 20°C) (rating)

[2] Vapour pressure (mPa @ 20 to 25°C)

[3] Persistence measured as average $DT_{50}$ (days for 50% decomposition) under field situations.

[4] Mobility in the soil – propensity for soil binding using average $K_{OC}$ value to determine rating

[#] Shaner D. (2014) Herbicide Handbook (2014) Weed Society of America

[@1] USDA Natural Resources Conservation Service. (n.d.) Windows Pesticide Screening Tool

[@2] National Registration Authority for Agricultural and Veterinary Chemicals. (2003) Evaluation of the new active mesosulfuron-methyl in the product Atlantis Selective Herbicide

[@3] Bayer CropScience. (2014). Hussar OD 2014 Plantback Guide

[@4] Bayer CropScience. (n.d.) Path and Drive Safety Data sheet

[@5] HerbiGuide Pty Ltd. (2014). Eclipse Herbicide

[@6] APVMA. (2008). Evaluation of the new active pyroxsulam in the product Crusader Herbicide

[@7] Imtrade. (2017). Edge 900WG Safety Data Sheet

[@8] APVMA. (2012). Evaluation of the new active saflufenacil in the product Sharpen WG Herbicide

[@9] APVMA. (2007. September). Evaluation of the new active pyrosulfotole in the product Precept Selective Herbicide

[@10] APVMA. (2017). Evaluation of the new active bicyclopyrone in the product Talinor Herbicide

[@11] Bayer CropScience. (2011). Balance herbicide technical guide

[@12] Dow AgroSciences. (2013). Arylex® active technical bulletin

[@13] APVMA. (2007. August). Evaluation of the active dimethenamid-P in the product Frontier-P Herbicide

[@14] APVMA. (2016). Evaluation of the new active metazachlor in the product Butisan Herbicide

[@15] APVMA. (2011). Evaluation of the new active pyroxasulfone in the Product Sakura® 850 WG Herbicide

[A] Paradigm is a mixture of florasulam and halauxifen-methyl

[B] Precept is a mixture of pyrasulfotole and MCPA

[C] Talinor is a mixture of bicyclopyrone and bromoxynil

[D] Hotshot is a mixture of aminopyralid and fluroxypyr

# FURTHER INFORMATION

## RE-CROPPING PERIODS FOR NSW

Fleming, J., McNee, T., Cook, T., & Manning, B. (2012). "Weed Control in Summer Crops 2012-13". NSW Department of Trade and Investment, Regional Infrastructure and Services http://www.dpi.nsw.gov.au/biosecurity/weeds/weed-control/management-guides/summer

Brooke, G., & McMaster, C. (2019). "Weed Control in Winter Crops". NSW Department of Primary Industries http://www.dpi.nsw.gov.au/agriculture/broadacre/guides/weed-control-winter-crops

## VIDEOS

GRDC: Pre-emergent Herbicides – Part 1 Solubility & Binding https://www.youtube.com/watch?v=s63GYYyflzw&t=1s

GRDC: Pre-emergent Herbicides – Part 2 Incorporation by Sowing https://www.youtube.com/watch?v=LJNjuMWS57U&t=1s

## ON-LINE LEARNING

WeedSmart Diversity Era: Pre-emergent Herbicides 101 https://www.diversityera.com/courses/pre-emergent-herbicides-101

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