GRDC COASTAL WEEDS WORKSHOPS

GRDC
GRAINS RESEARCH & DEVELOPMENT CORPORATION

grdc.com.au

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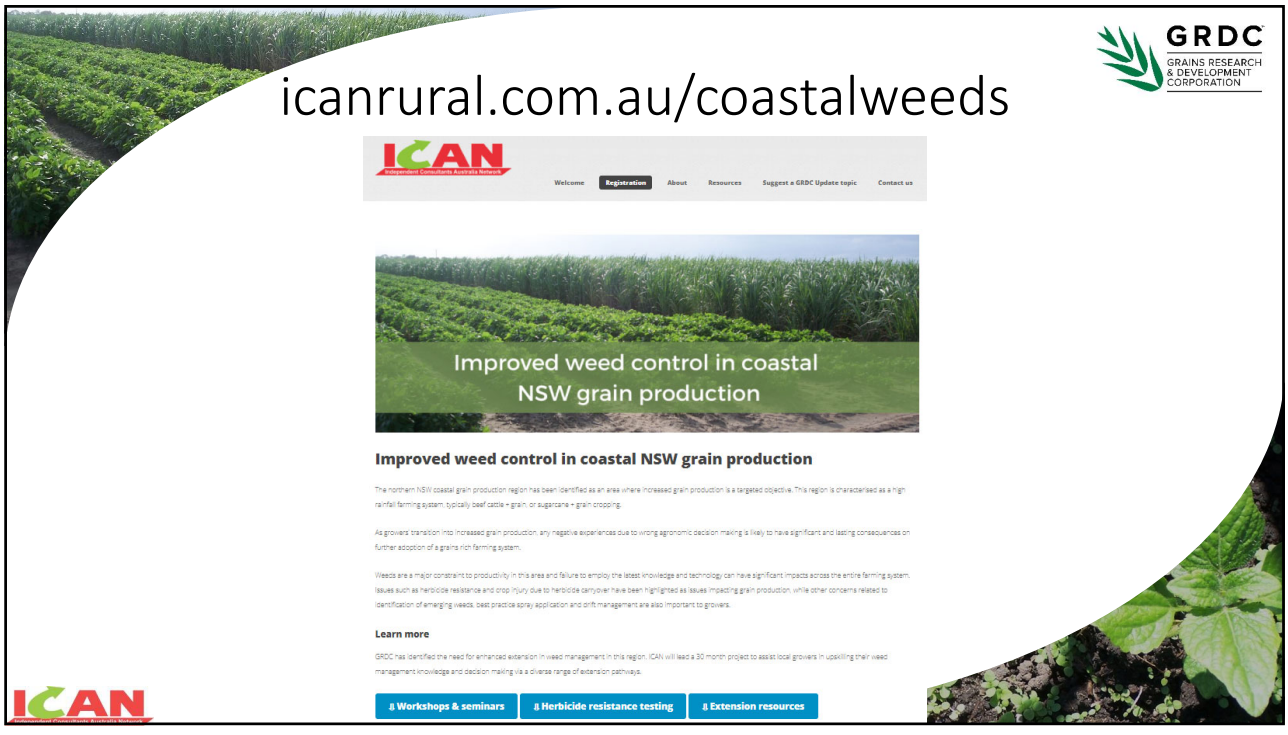
1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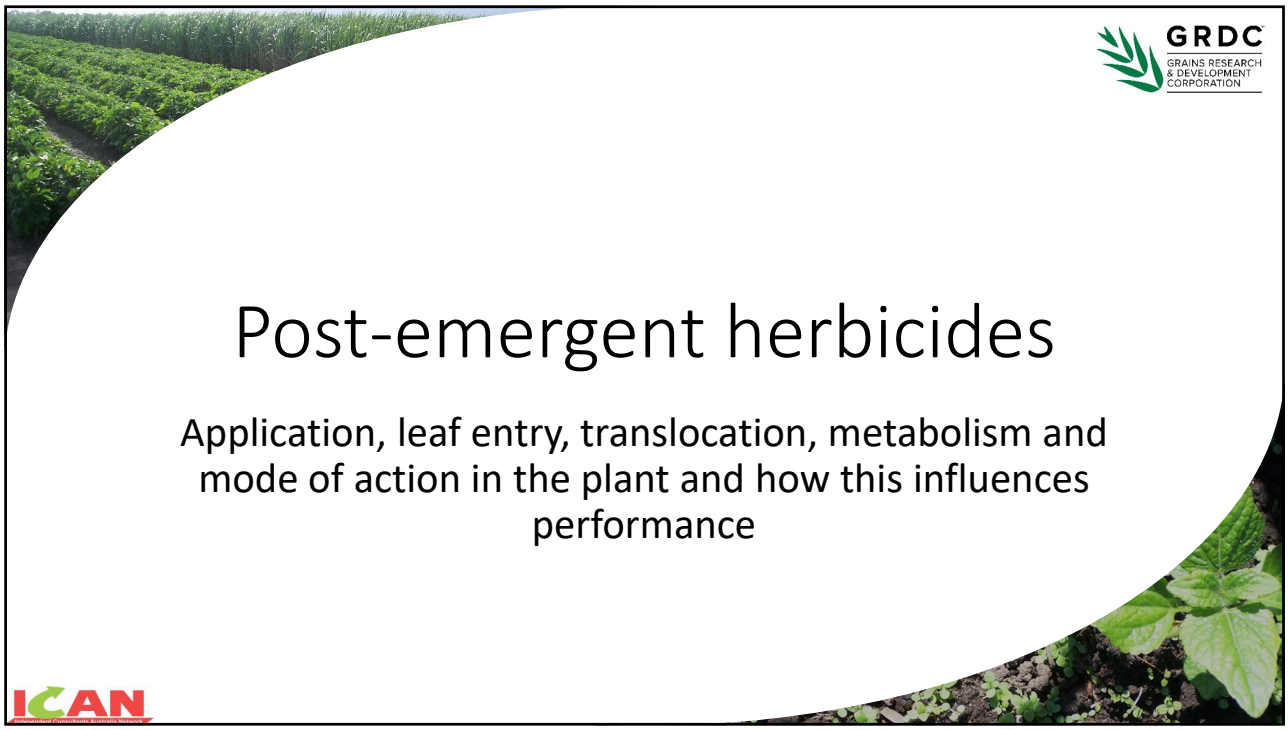

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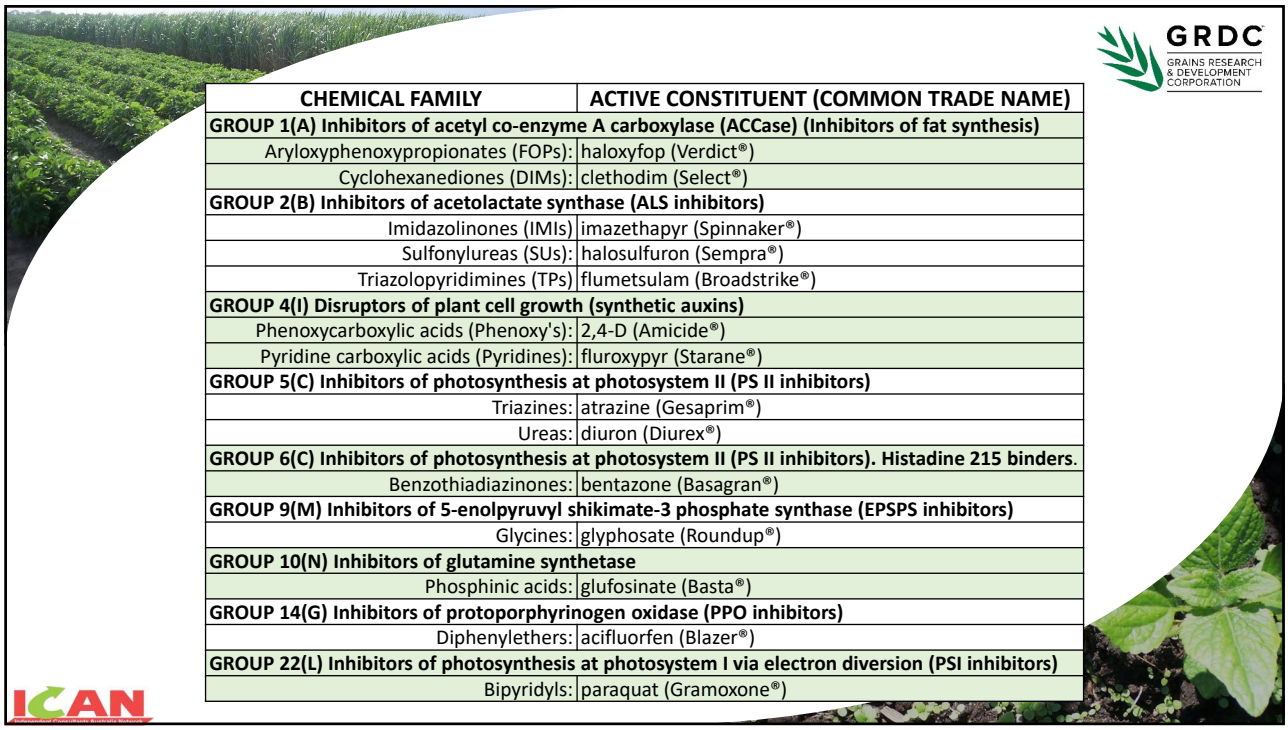
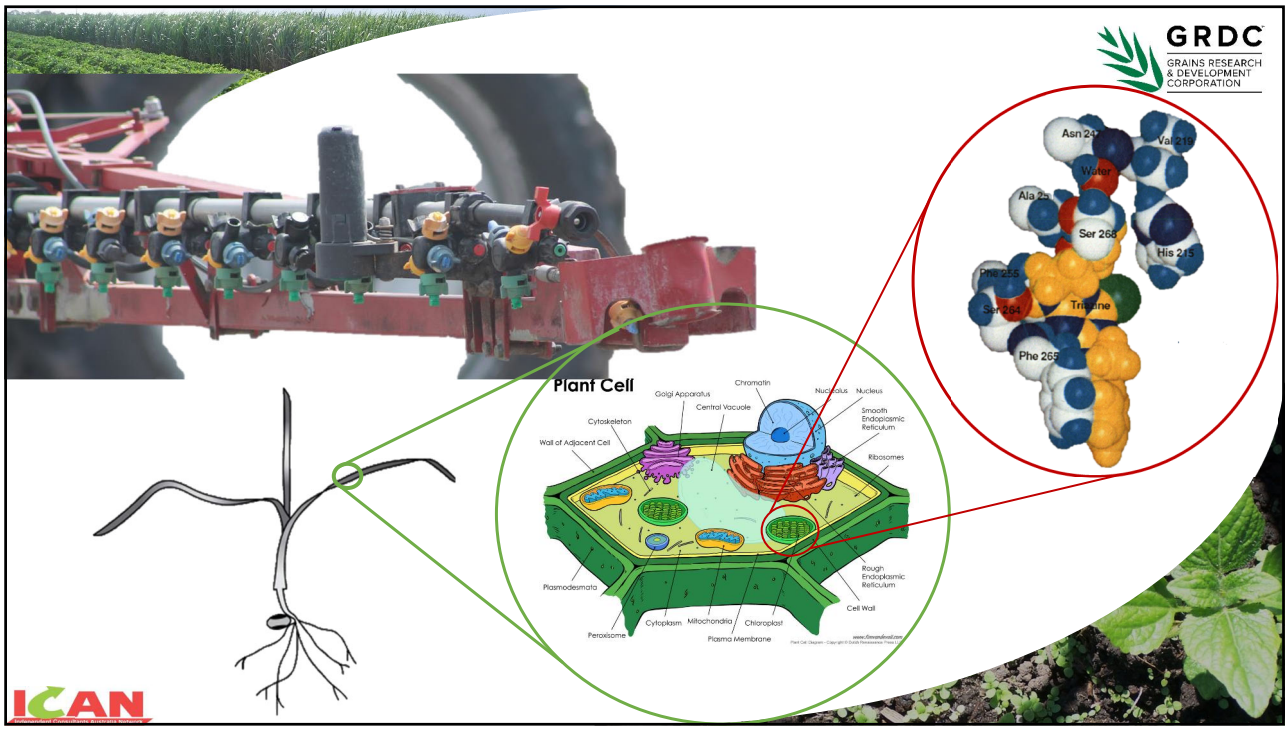


CHEMICAL FAMILY	ACTIVE CONSTITUENT (COMMON TRADE NAME)
GROUP 1(A) Inhibitors of acetyl co-enzyme A carboxylase (ACCase) (Inhibitors of fat synthesis)	
Aryloxyphenoxypropionates (FOPs):	haloxyfop (Verdict®)
Cyclohexanediones (DIMs):	clethodim (Select®)
GROUP 2(B) Inhibitors of acetolactate synthase (ALS inhibitors)	
Imidazolinones (IMIs)	imazethapyr (Spinnaker®)
Sulfonylureas (SUs):	halosulfuron (Sempra®)
Triazolopyridimines (TPs)	flumetsulam (Broadstrike®)
GROUP 4(I) Disruptors of plant cell growth (synthetic auxins)	
Phenoxycarboxylic acids (Phenoxy's):	2,4-D (Amicide®)
Pyridine carboxylic acids (Pyridines):	fluroxypyr (Starane®)
GROUP 5(C) Inhibitors of photosynthesis at photosystem II (PS II inhibitors)	
Triazines:	atrazine (Gesaprim®)
Ureas:	diuron (Diurex®)
GROUP 6(C) Inhibitors of photosynthesis at photosystem II (PS II inhibitors). Histadine 215 binders.	
Benzothiadiazinones:	bentazone (Basagran®)
GROUP 9(M) Inhibitors of 5-enolpyruvyl shikimate-3 phosphate synthase (EPSPS inhibitors)	
Glycines:	glyphosate (Roundup®)
GROUP 10(N) Inhibitors of glutamine synthetase	
Phosphinic acids:	glufosinate (Basta®)
GROUP 14(G) Inhibitors of protoporphyrinogen oxidase (PPO inhibitors)	
Diphenylethers:	acifluorfen (Blazer®)
GROUP 22(L) Inhibitors of photosynthesis at photosystem I via electron diversion (PSI inhibitors)	
Bipyridyls:	paraquat (Gramoxone®)

4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Asn 247
Val 219
Water
Ala 251
Ser 264
His 215
Phe 255
Ser 264
Triazine
Phe 265
Plant Cell
Golgi Apparatus
Chromatin
Nucleolus
Nucleus
Central Vacuole
Smooth Endoplasmic Reticulum
Cytoskeleton
Wall of Adjacent Cell
Ribosomes
Plasmodesmata
Rough Endoplasmic Reticulum
Cell Wall
Peroxisome
Cytoplasm
Mitochondria
Chloroplast
Plasma Membrane
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Application & leaf entry
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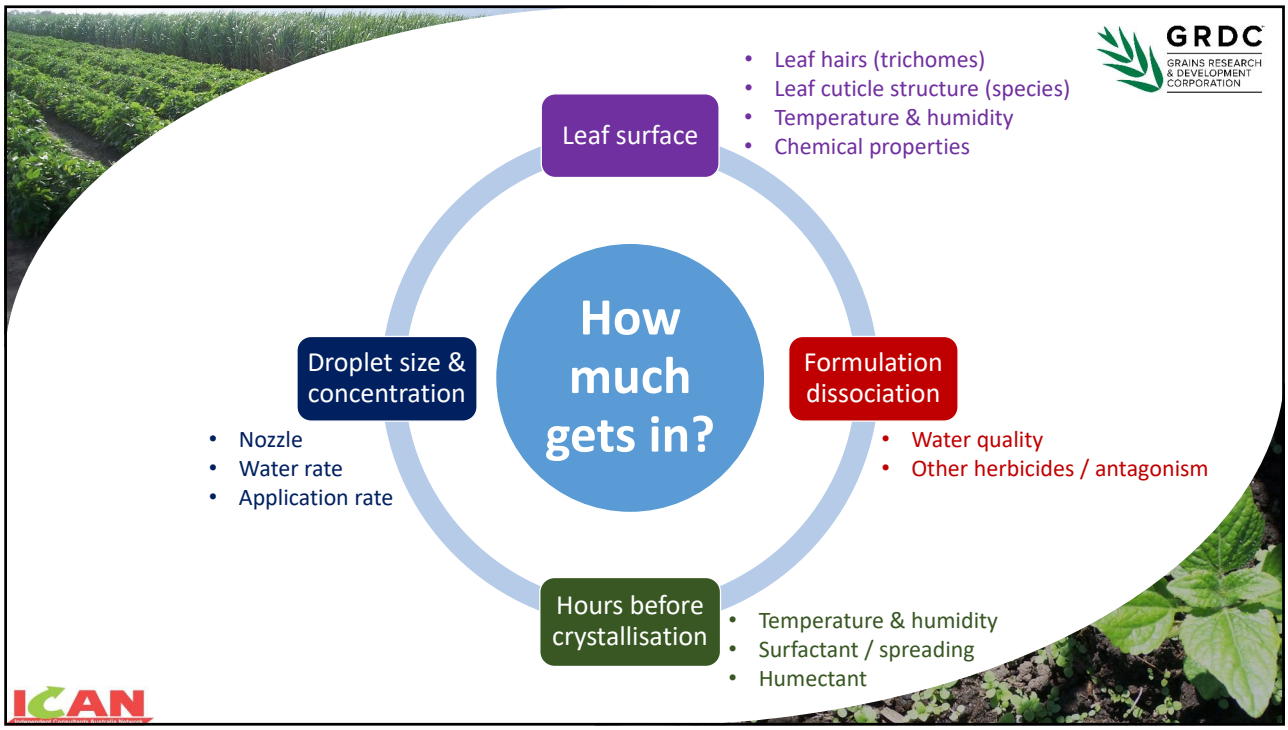

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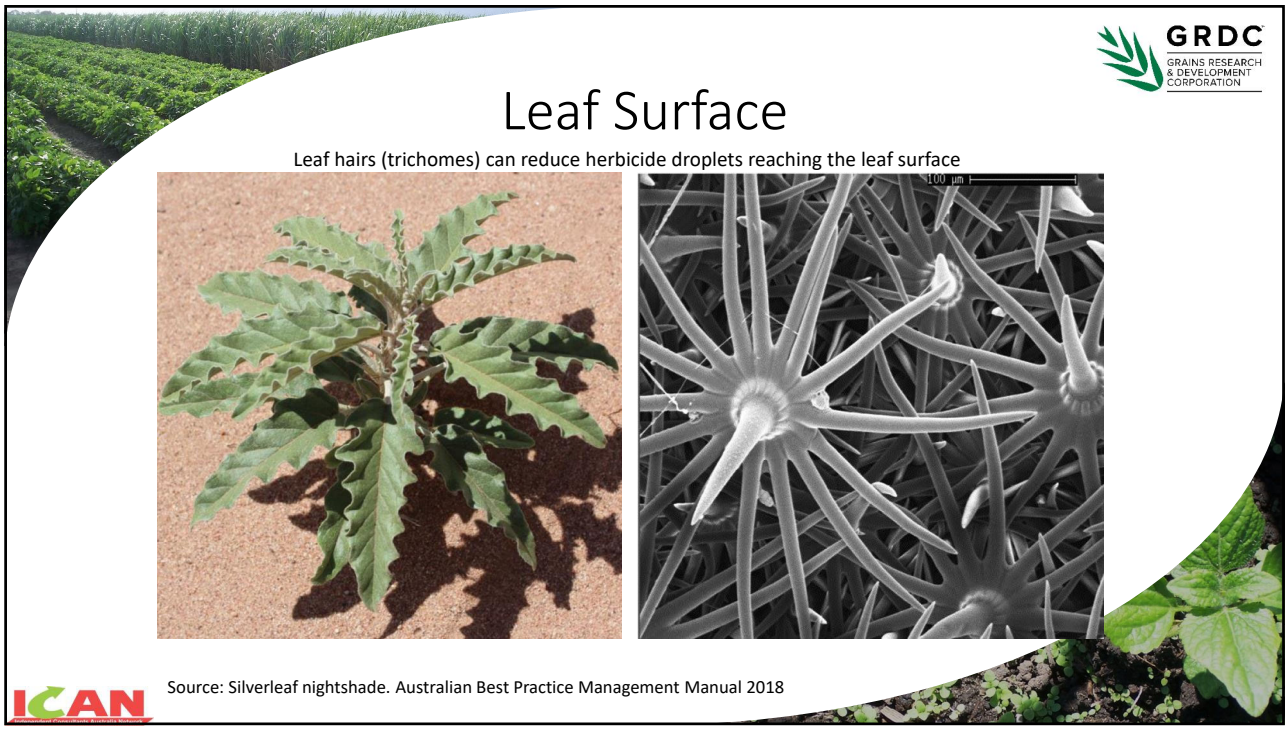

Source: Silverleaf nightshade. Australian Best Practice Management Manual 2018

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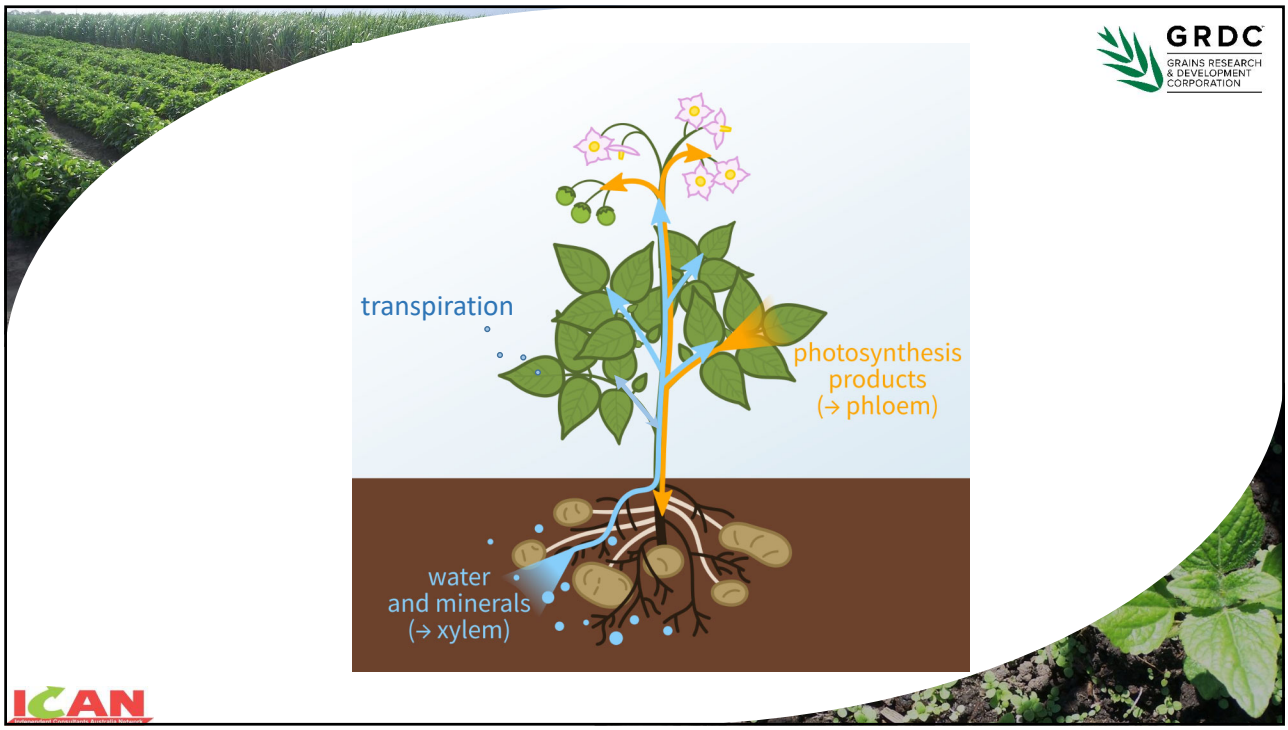
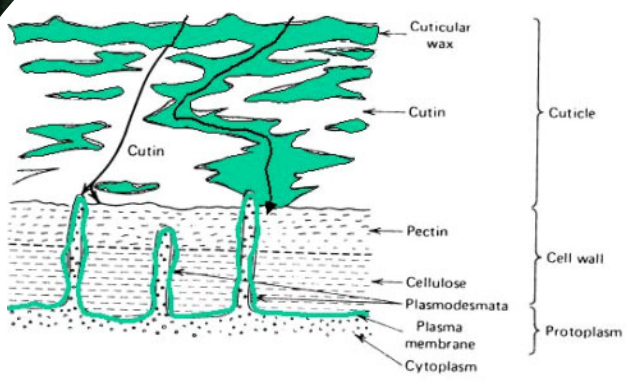


9

Penetrating the cuticle



Absorption route from leaf surface to cytoplasm (Ashton & Crafts, 1981)

Hydrophilic (water loving) herbicides

- Slow to penetrate waxy cuticle.
- Require hours on leaf surface.
- Movement increases after leaf entry

Lipophilic (fat loving) herbicides

- Fast entry of the waxy cuticle
- Then movement slows as environment becomes more aqueous

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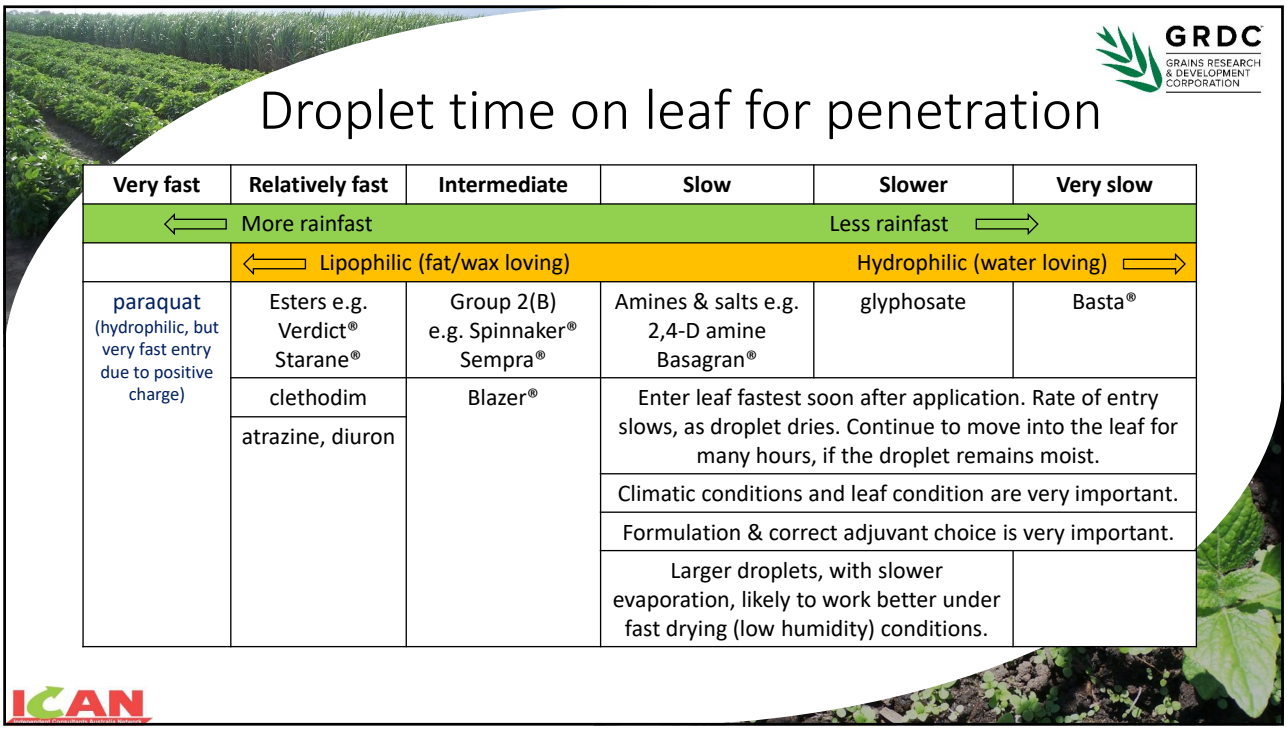
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Droplet time on leaf for penetration
Very fast
Relatively fast
Intermediate
Slow
Slower
Very slow
More rainfast
Less rainfast
Lipophilic (fat/wax loving)
Hydrophilic (water loving)
paraquat (hydrophilic, but very fast entry due to positive charge)
Esters e.g. Verdict® Starane®
Group 2(B) e.g. Spinnaker® Sempra®
Amines & salts e.g. 2,4-D amine Basagran®
glyphosate
Basta®
clethodim
Blazer®
atrazine, diuron
Enter leaf fastest soon after application. Rate of entry slows, as droplet dries. Continue to move into the leaf for many hours, if the droplet remains moist.
Climatic conditions and leaf condition are very important.
Formulation & correct adjuvant choice is very important.
Larger droplets, with slower evaporation, likely to work better under fast drying (low humidity) conditions.
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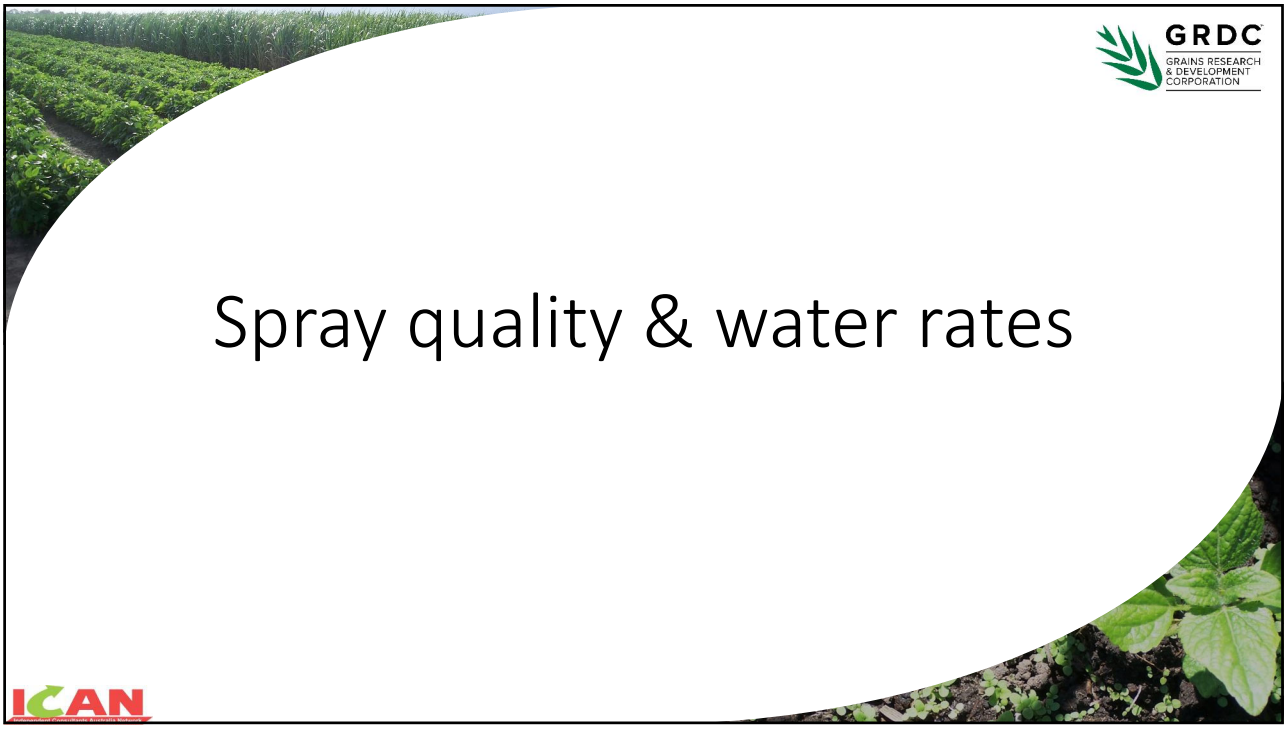
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Spray quality & water rates
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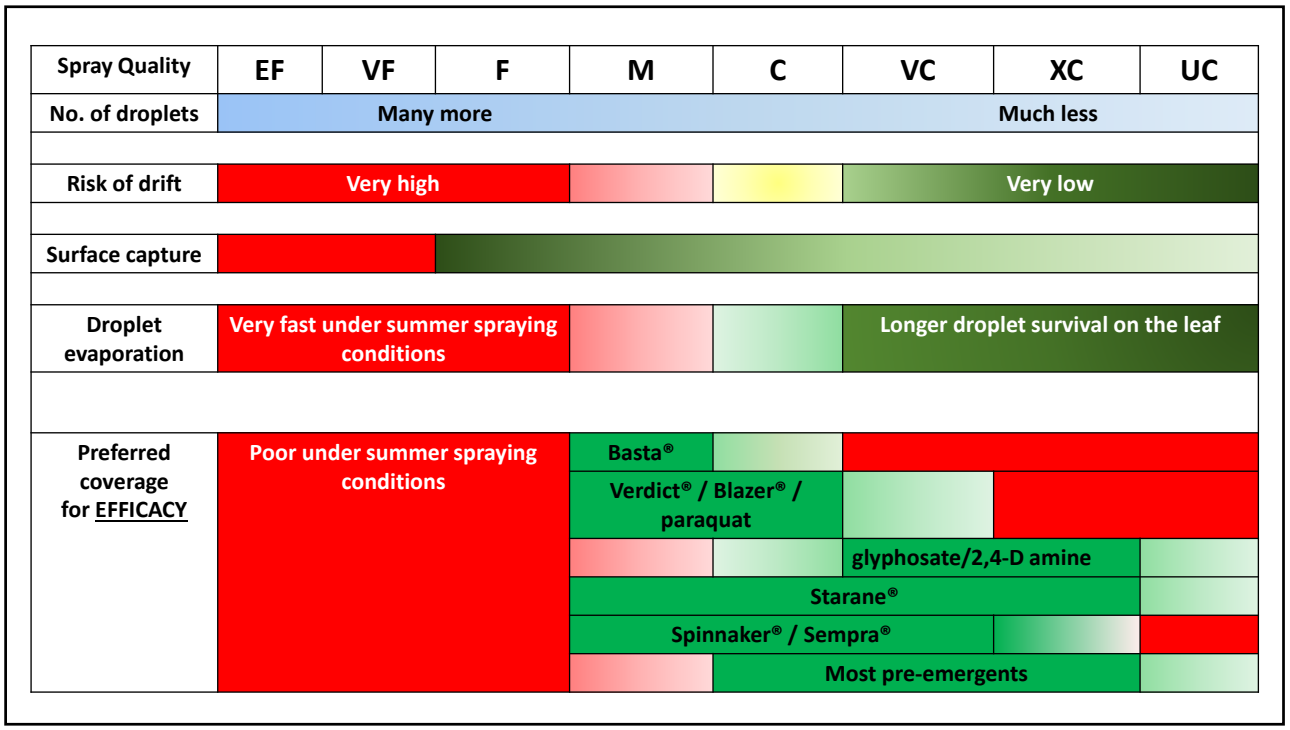
Spray Quality
EF
VF
F
M
C
VC
XC
UC
No. of droplets
Many more
Much less
Risk of drift
Very high
Very low
Surface capture
Droplet evaporation
Very fast under summer spraying conditions
Longer droplet survival on the leaf
Preferred coverage for EFFICACY
Poor under summer spraying conditions
Basta®
Verdict® / Blazer® / paraquat
glyphosate/2,4-D amine
Starane®
Spinnaker® / Sempra®
Most pre-emergents

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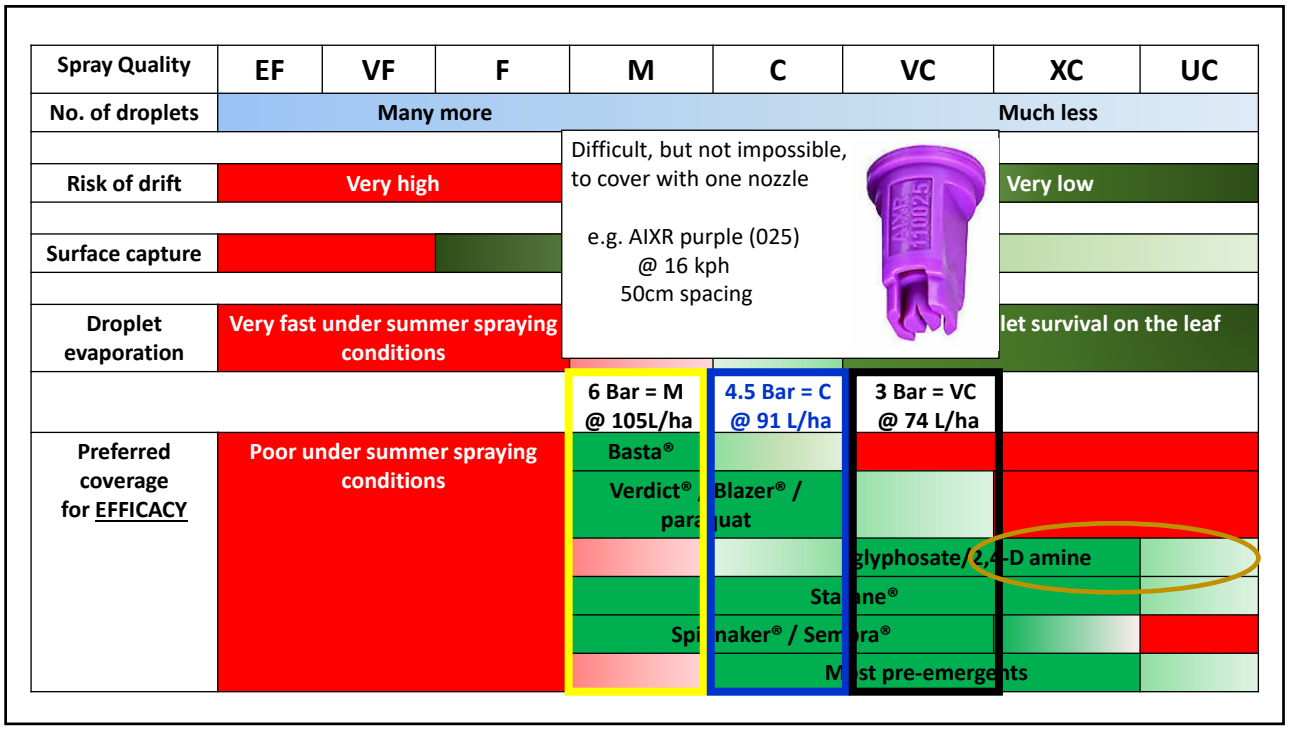
Spray Quality
EF
VF
F
M
C
VC
XC
UC
No. of droplets
Many more
Much less
Difficult, but not impossible, to cover with one nozzle
e.g. AIXR purple (025)
@ 16 kph
50cm spacing
Risk of drift
Very high
Very low
Surface capture
Droplet evaporation
Very fast under summer spraying conditions
6 Bar = M @ 105L/ha
4.5 Bar = C @ 91 L/ha
3 Bar = VC @ 74 L/ha
Preferred coverage for EFFICACY
Poor under summer spraying conditions
Basta®
Verdict® / Blazer® / paraquat
glyphosate/2,4-D amine
Starane®
Spinnaker® / Sempra®
Most pre-emergents

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Where do the herbicide MOAs work in the plant?

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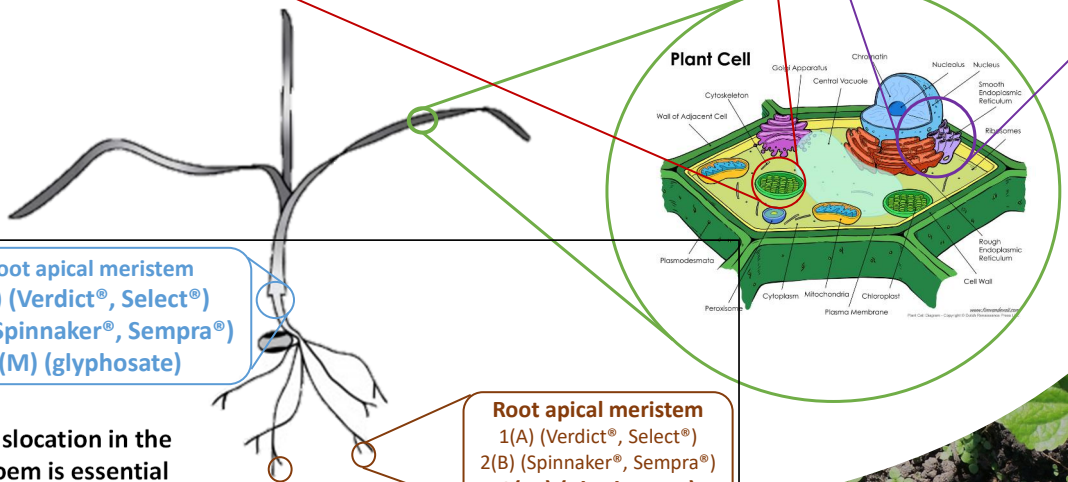
Contact herbicides

Chloroplast
5(C) (atrazine, diuron) **6(C) (Basagran®)**
10(N) (Basta®) **14 (G) (Blazer®)**
22(L) (Gramoxone®)
2(B) (Spinnaker®, Sempra®) 9(M) (glyphosate)

Nucleus, endoplasmic reticulum, plasma membrane
4(I) (2,4-D, Starane®)
All cells throughout the plant – translocation required



Shoot apical meristem
1(A) (Verdict®, Select®)
2(B) (Spinnaker®, Sempra®)
9(M) (glyphosate)

Translocation in the phloem is essential

Root apical meristem
1(A) (Verdict®, Select®)
2(B) (Spinnaker®, Sempra®)
9(M) (glyphosate)

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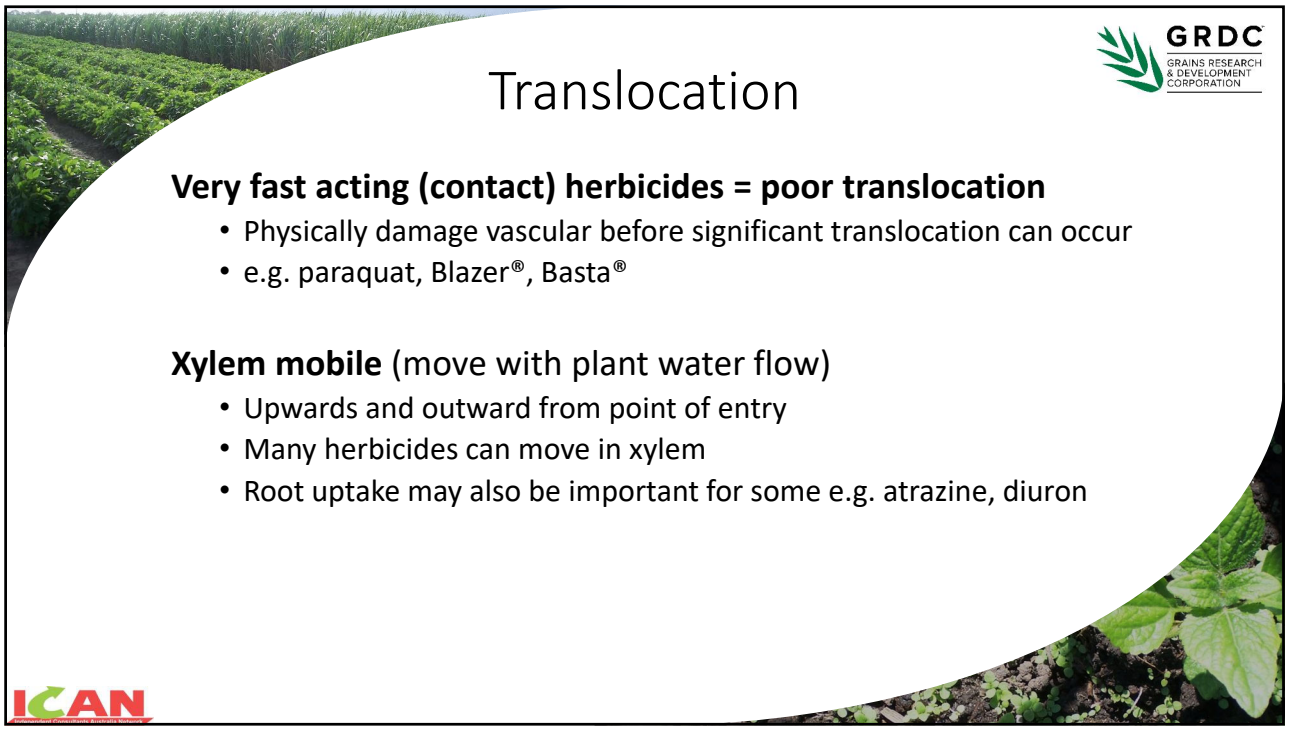
Translocation
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Very fast acting (contact) herbicides = poor translocation
• Physically damage vascular before significant translocation can occur
• e.g. paraquat, Blazer®, Basta®
Xylem mobile (move with plant water flow)
• Upwards and outward from point of entry
• Many herbicides can move in xylem
• Root uptake may also be important for some e.g. atrazine, diuron
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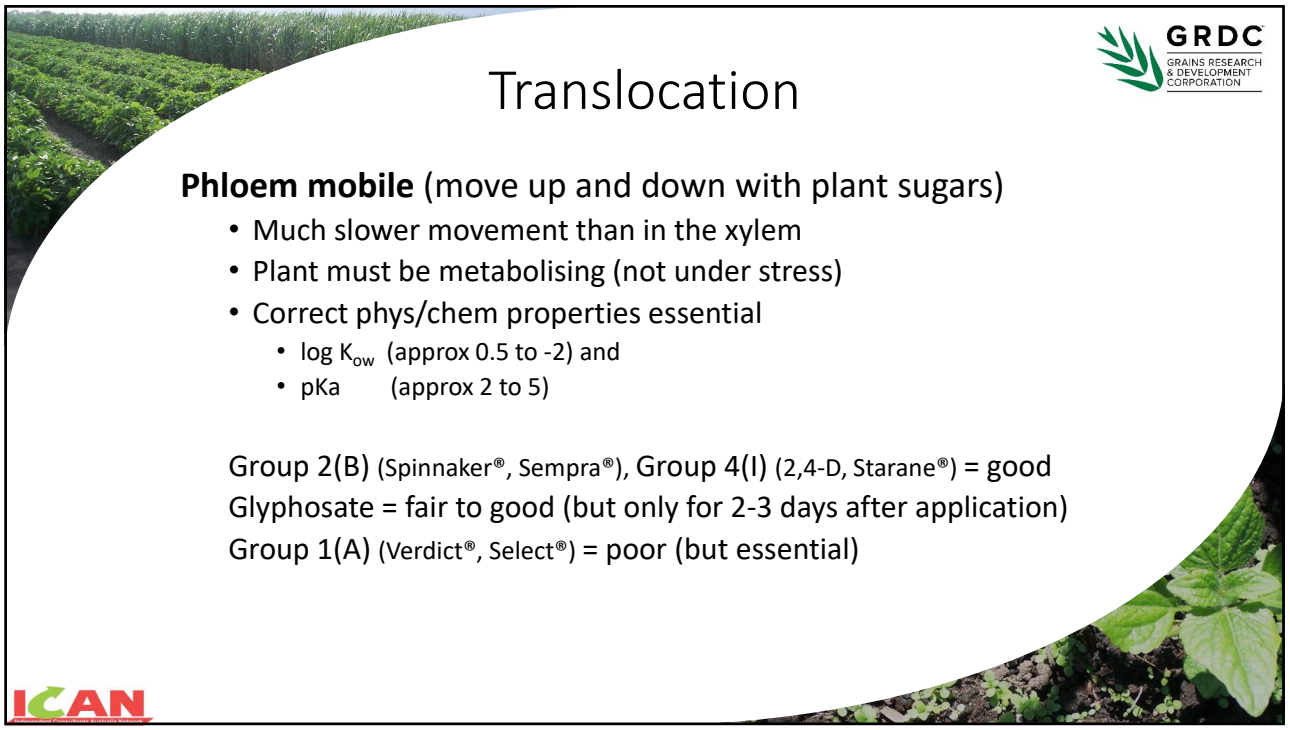
Translocation
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Phloem mobile (move up and down with plant sugars)
• Much slower movement than in the xylem
• Plant must be metabolising (not under stress)
• Correct phys/chem properties essential
• log K_{ow} (approx 0.5 to -2) and
• pKa (approx 2 to 5)
Group 2(B) (Spinnaker®, Sempra®), Group 4(I) (2,4-D, Starane®) = good
Glyphosate = fair to good (but only for 2-3 days after application)
Group 1(A) (Verdict®, Select®) = poor (but essential)
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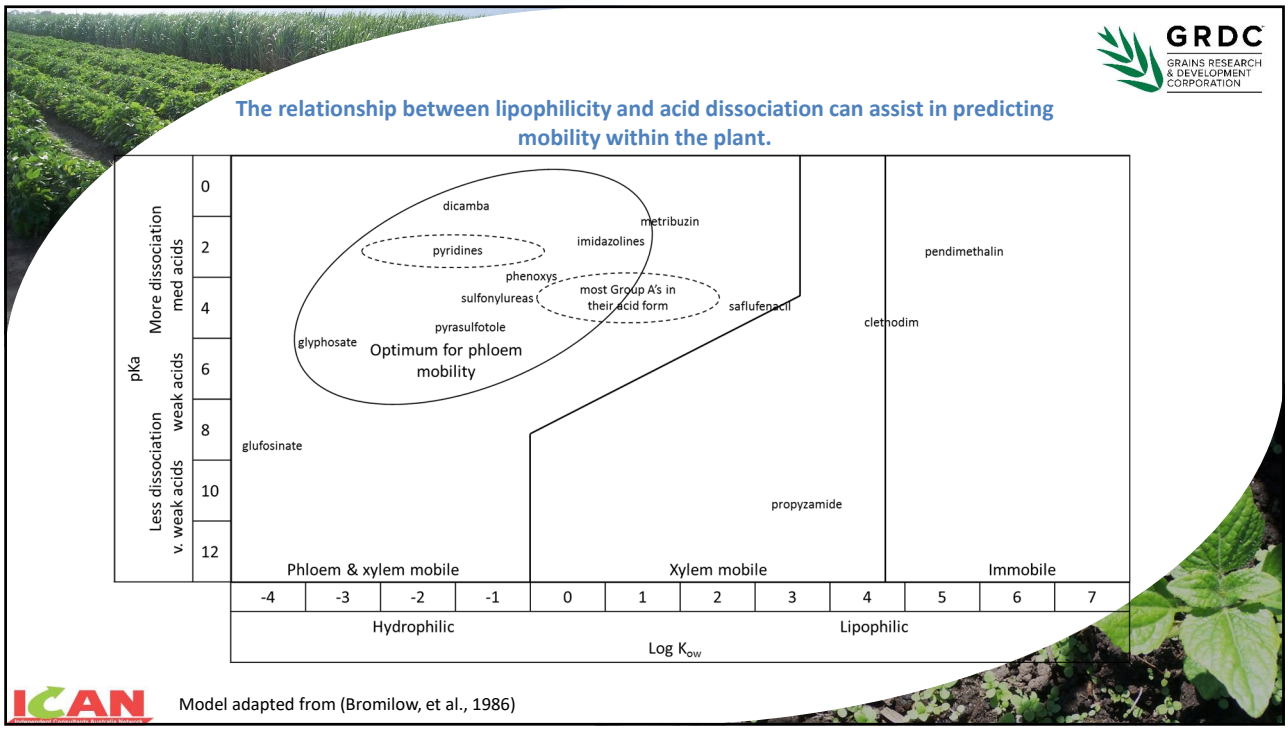
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The relationship between lipophilicity and acid dissociation can assist in predicting mobility within the plant.
pKa
More dissociation med acids
Less dissociation v. weak acids
weak acids
0
2
4
6
8
10
12
dicamba
metribuzin
pyridines
imidazolines
phenoxys
sulfonylureas
most Group A's in their acid form
saflufenacil
pendimethalin
clethodim
pyrasulfotole
glyphosate
Optimum for phloem mobility
glufosinate
propyzamide
Phloem & xylem mobile
Xylem mobile
Immobile
-4
-3
-2
-1
0
1
2
3
4
5
6
7
Hydrophilic
Lipophilic
Log K_{ow}
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Model adapted from (Bromilow, et al., 1986)

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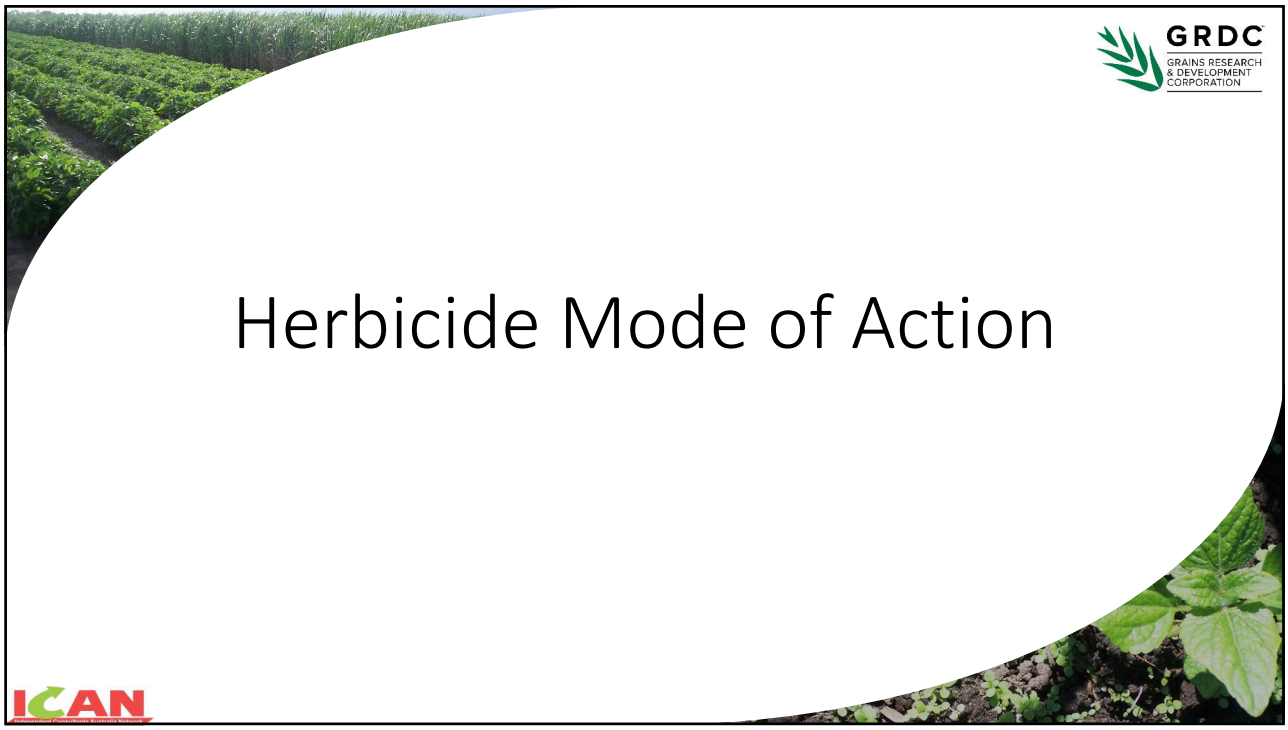
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Herbicide Mode of Action
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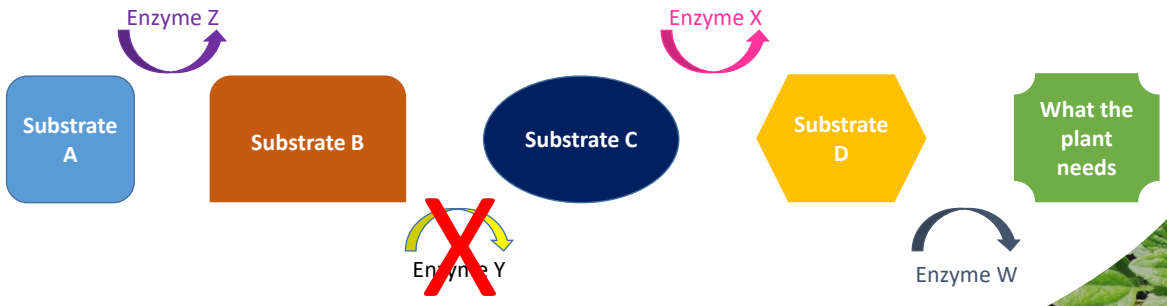
How do post-em herbicides work?

Most herbicide modes of action disrupt an enzyme process



Herbicide blocks an enzyme step.

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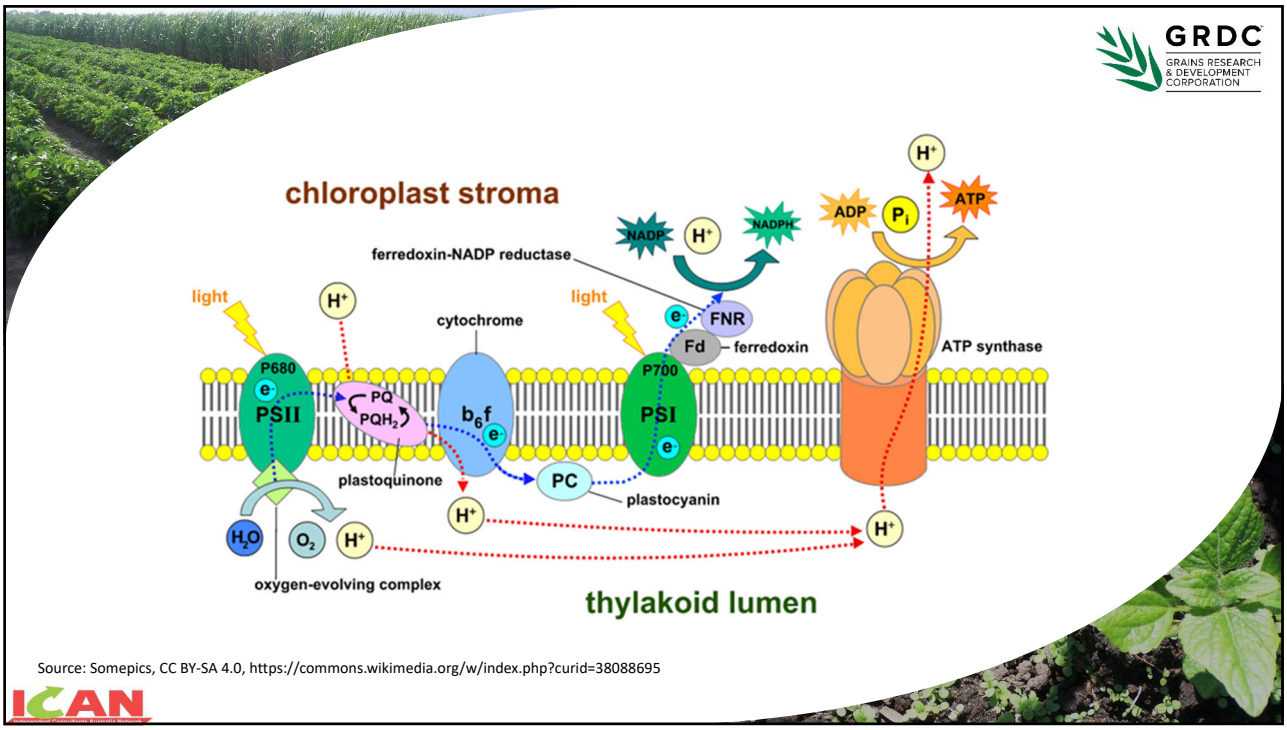

Source: Somepics, CC BY-SA 4.0, https://commons.wikimedia.org/w/index.php?curid=38088695

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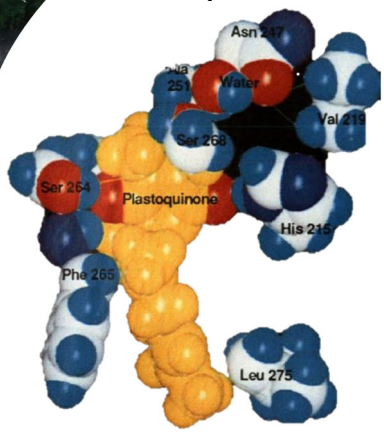
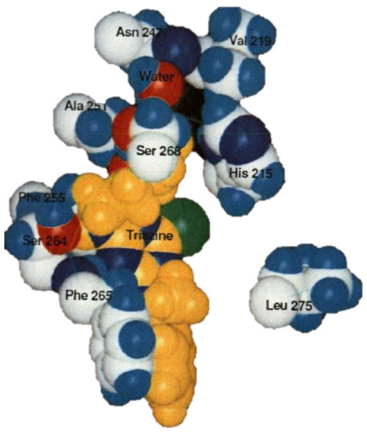
Group 5(C) binding site

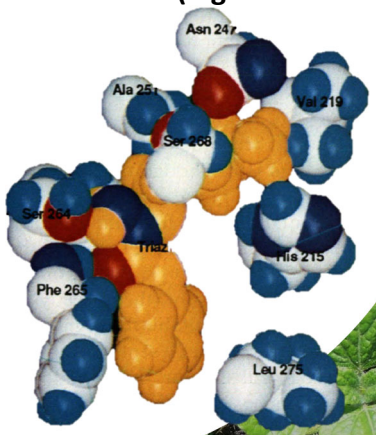
Plastoquinone



Triazines (e.g. atrazine)



Triazinones (e.g. metribuzin)



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Metabolism

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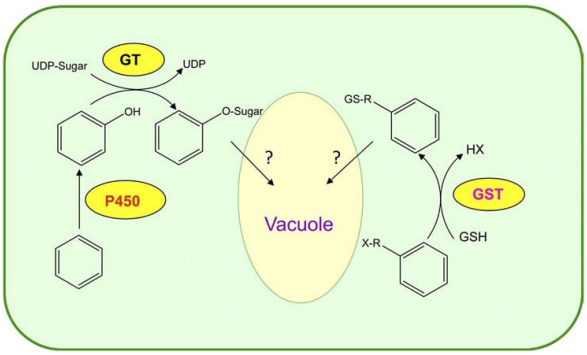
Metabolism

Selective herbicides

- Metabolic pathways degrade the herbicide within the crop before reaching the target site
- Weed selectivity is often also a function of metabolism



- Key metabolic super-families
  - Cytochrome P450's monooxygenase
  - Glucosyl transferase
  - Glutathione S-transferase

Plant Physiol. 2014 Nov; 166(3): 1106–1118.

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Selectivity depends on

- Species (level of metabolic enzymes)
- Actively metabolising (no stress)
- Application rate
- Speed of cell entry
  - Leaf entry / adjuvant / translocation

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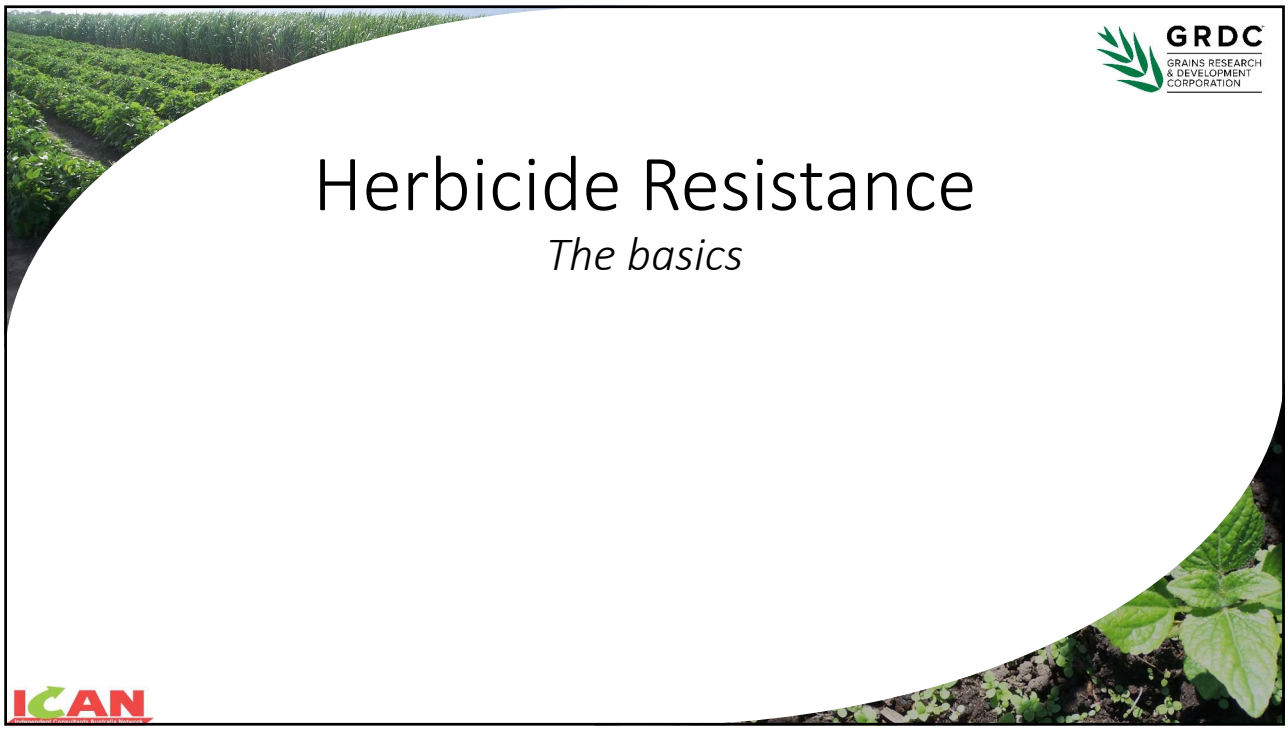
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Herbicide Resistance
The basics
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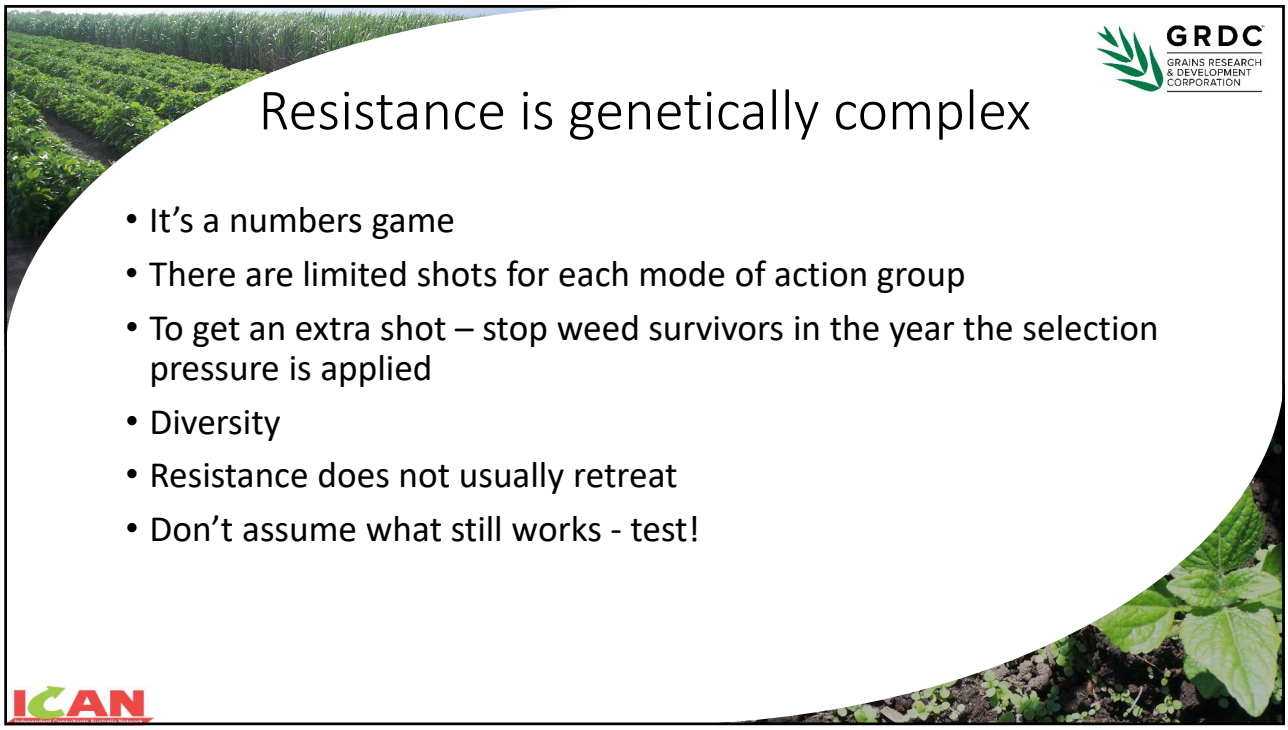
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Resistance is genetically complex
• It's a numbers game
• There are limited shots for each mode of action group
• To get an extra shot – stop weed survivors in the year the selection pressure is applied
• Diversity
• Resistance does not usually retreat
• Don't assume what still works - test!
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Non- target site resistance

Herbicide is prevented from getting to the target site in the full dose.

May often look like a sub-lethal rate was applied.

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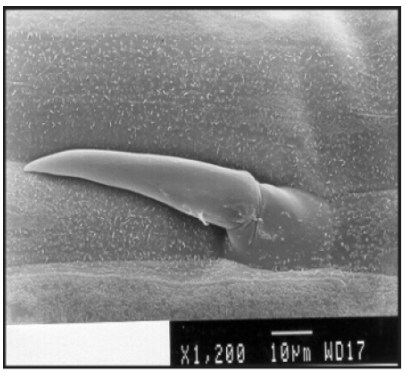
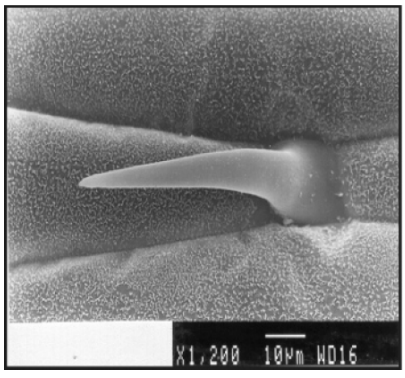
Plant changes

- Leaf structure changed to reduce herbicide penetration





Scanning electron micrographs of the adaxial outer surface of the susceptible (left) and resistant (right) biotypes of *Lolium rigidum*, indicating greater epicuticular wax density in the resistant biotype.

Prado et al (2005) *Lolium rigidum*, a Pool of Resistance Mechanisms to ACCase Inhibitor Herbicides

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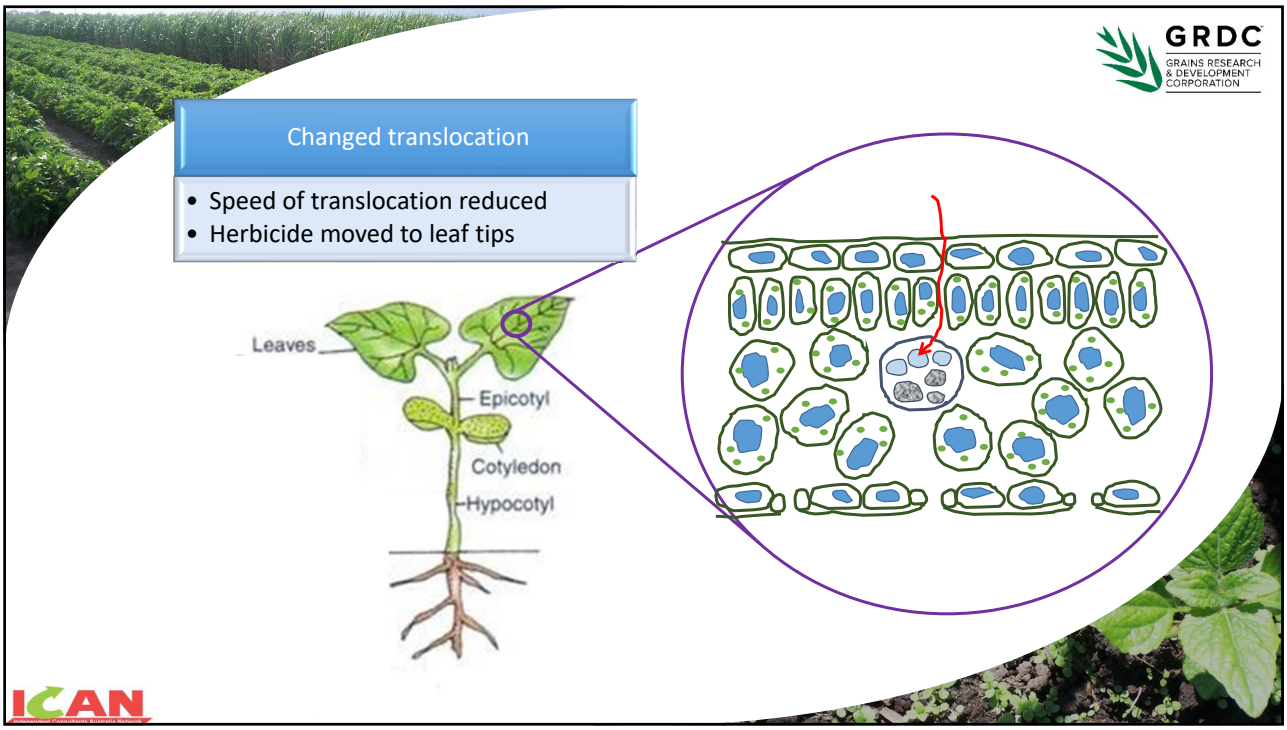
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Changed translocation
• Speed of translocation reduced
• Herbicide moved to leaf tips
Leaves
Epicotyl
Cotyledon
Hypocotyl
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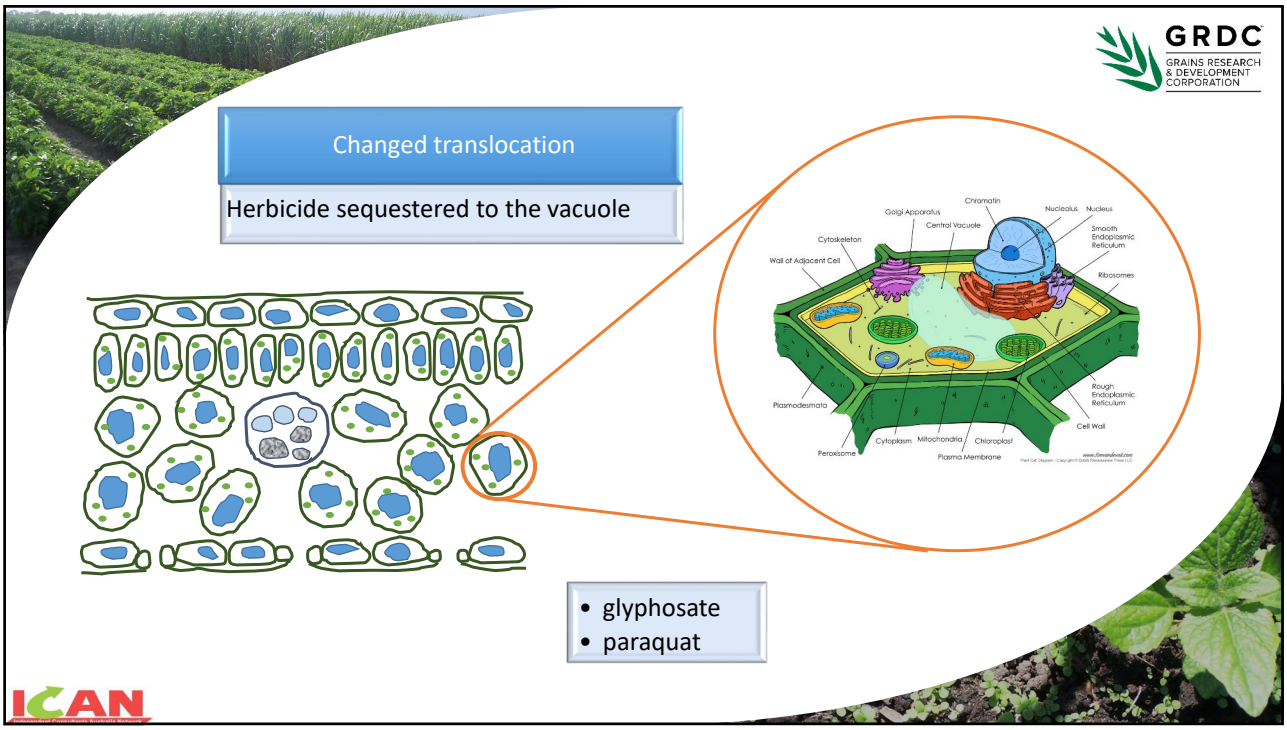
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Changed translocation
Herbicide sequestered to the vacuole
Chromatin
Golgi Apparatus
Nucleolus
Nucleus
Central Vacuole
Cytoskeleton
Smooth Endoplasmic Reticulum
Wall of Adjacent Cell
Ribosomes
Plasmodesmata
Rough Endoplasmic Reticulum
Cell Wall
Peroxisome
Cytoplasm
Mitochondria
Chloroplast
Plasma Membrane
• glyphosate
• paraquat
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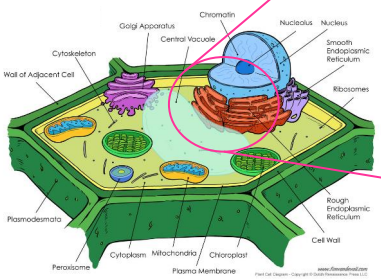
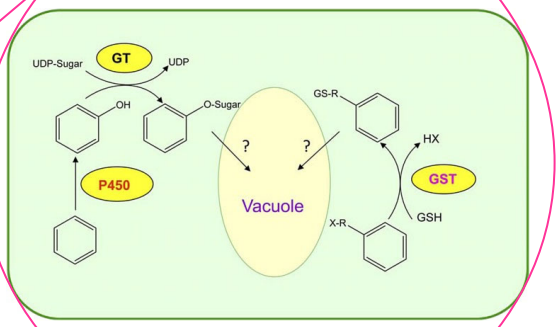
Metabolic

Herbicide is degraded (via P450s or GSTs) before reaching the target site





- Can have cross-resistance across MOA groups

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Target site resistance

Herbicide reaches the target site, but performance is impaired

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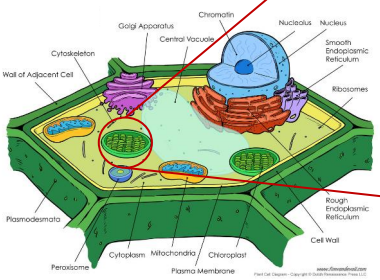
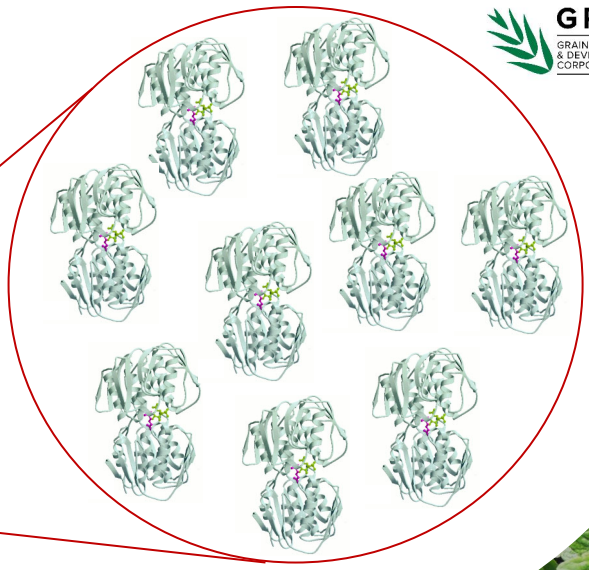
Gene amplification

Plant creates multiple copies of the gene





Glyphosate only (to date)

Glyphosate binding site Schonbrunn et.al. (2001) www.pnas.org/content/98/4/1376

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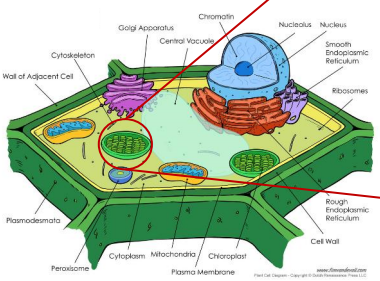
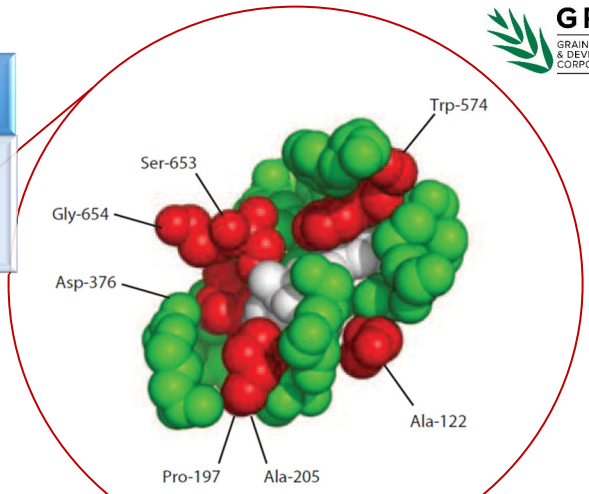
Target site mutation

- Mutation of the target site prevents herbicide from binding
- Many different mutations may exist





- No cross-resistance across MOA groups
- May be differences within a MOA group
  e.g. FOPs v DIMs; SU versus IMI

36

Target site substitution

Group A	Group B	Group C
7 locations, 11 substitutions	**8 locations, 26 substitutions**	**7 locations, 8 substitutions**
Ile-1781-Leu Ile-1781-Val Trp-1999-Cys Trp-1999-Leu Trp-2027-Cys Ile-2041-Asn Ile-2041-Val Asp-2078-Gly Cys-2088-Arg Gly-2096-Ala Gly-2096-Ser	Ala-122-Val Ala-122-Thr Ala-122-Tyr Pro-197-Thr Pro-197-His Pro-197-Arg Pro-197-Leu Pro-197-Gln Pro-197-Glu Pro-197-Ser Pro-197-Ala Pro-197-Ile Pro-197-Tyr Pro-197-Asn Ala-205-Val Ala-205-Phe Asp-376-Glu Arg-377-His Trp-574-Leu Trp-574-Gly Trp-574-Met Ser-653-Ile Ser-653-Thr Ser-653-Asn Gly-654-Glu Gly-654-Asp	Leu-218-Val Val-219-Ile Ala-251-Val Phe-255-Ile Ser-264-Gly Ser-264-Thr Asn-266-Thr Phe-274-Val

glyphosate
1 main location (106) + 2 secondary locations, 7 substitutions
Pro-106-Ser (2-8x) Pro-106-Ala (5-15x) Pro-106-Thr (3-11x) Pro-106-Leu (2x) Thr-102-Ser (3x) Pro-106-Ser + Pro-106-Leu (16-21x) Pro-106-Ser + Thr-102-Ile (180x) Pro-106-Ser + Thr-102-Ile + Ala-103-Val (314x)

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Maximising performance

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Group 1(A)

e.g. Verdict® (haloxyfop), Select® (clethodim)

Inhibits acetyl-CoA carboxylase (ACCase)

Key first step in fatty acid production

- Used for building cell membranes
- Mostly produced in crown of young plants.

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Group 1(A)
ACCase inhibitors

Leaf entry

Clethodim (e.g. Select®) moderately lipophilic

Verdict formulated as ester – lipophilic in applied form

- Hydrolyses to acid once inside the leaf

Lipophilic herbicides

- Enter leaf quickly = good rainfastness
- Respond strongly to crop oil concentrates (COC) e.g. Uptake®, Hasten® etc.

40

Group 1(A)
ACCase inhibitors

Translocation

Needs to move to the crown of the weed = phloem movement required

- Must be actively growing (translocating)

'Ion trapping' – large % of herbicide trapped within cells in leaf

Small weeds

- Less distance to move
- Fewer leaf cells to trap herbicide
- Producing more ACCase
  - (ACCase production reduces when weeds start to flower)

41

Group 1(A)
ACCase inhibitors

Tank mixing

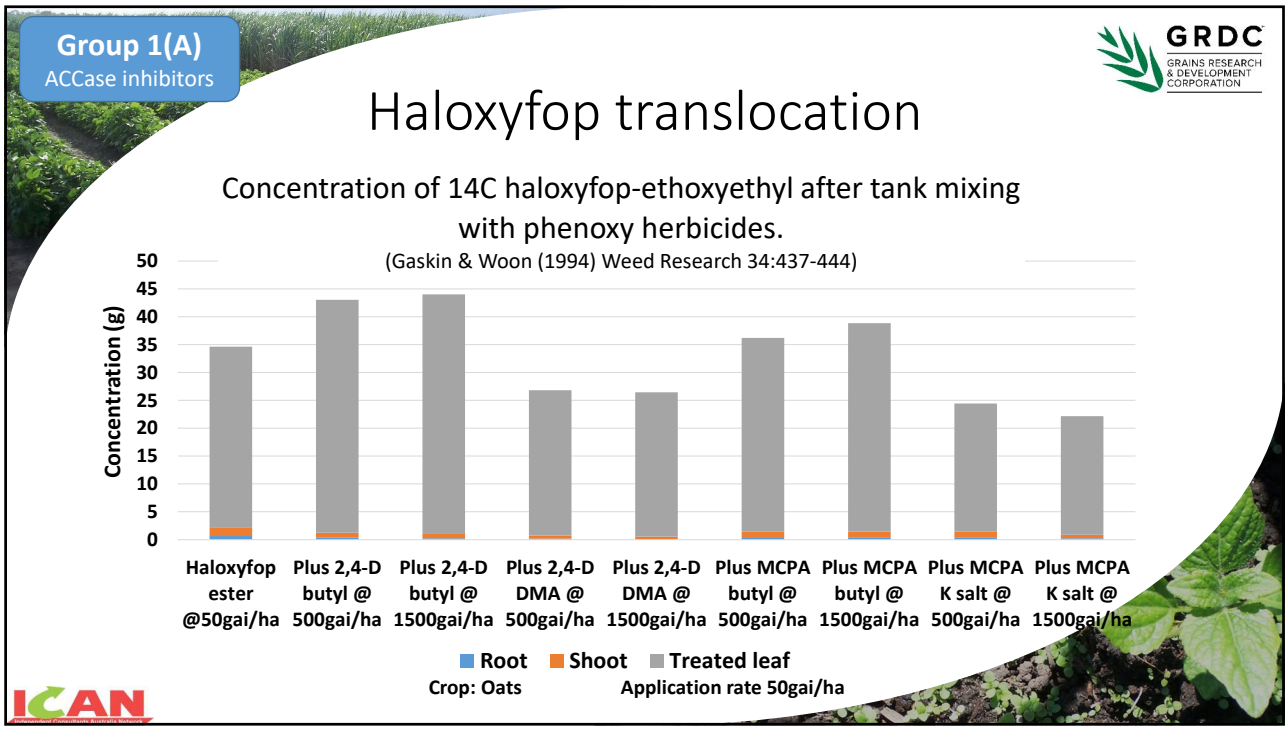
Group 4(I)

- Amines may reduce leaf uptake
- Amines and esters = faster metabolism within the plant

⇒**Less herbicide reaches the crown of the plant**

2,4-D > MCPA > pyridines (fluroxypyr / clopyralid / picloram)

42


Group 1(A)
ACCase inhibitors
GRDC
GRAINS RESEARCH & DEVELOPMENT CORPORATION
Haloxyfop translocation
Concentration of 14C haloxyfop-ethoxyethyl after tank mixing with phenoxy herbicides.
(Gaskin & Woon (1994) Weed Research 34:437-444)
Concentration (g)
50
45
40
35
30
25
20
15
10
5
0
Haloxyfop ester @50gai/ha
Plus 2,4-D butyl @ 500gai/ha
Plus 2,4-D butyl @ 1500gai/ha
Plus 2,4-D DMA @ 500gai/ha
Plus 2,4-D DMA @ 1500gai/ha
Plus MCPA butyl @ 500gai/ha
Plus MCPA butyl @ 1500gai/ha
Plus MCPA K salt @ 500gai/ha
Plus MCPA K salt @ 1500gai/ha
Root
Shoot
Treated leaf
Crop: Oats
Application rate 50gai/ha
ICAN

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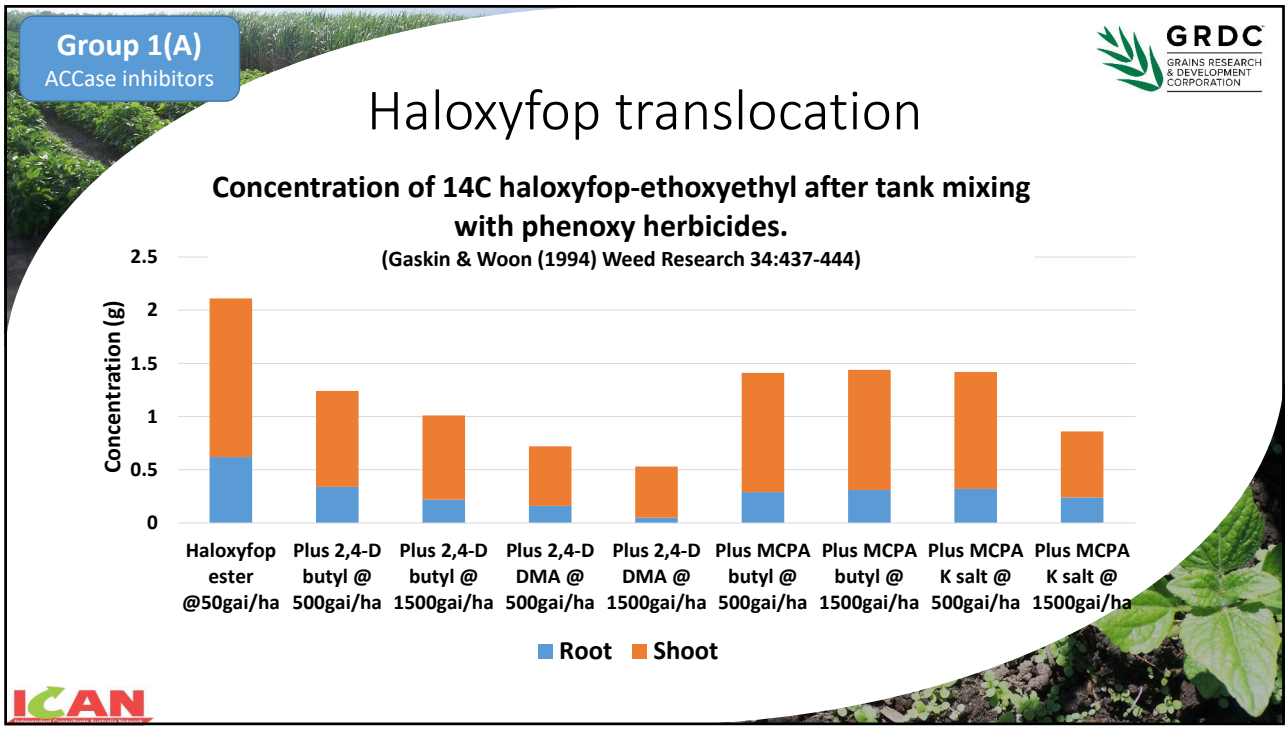
Group 1(A)
ACCase inhibitors
GRDC
GRAINS RESEARCH & DEVELOPMENT CORPORATION
Haloxyfop translocation
Concentration of 14C haloxyfop-ethoxyethyl after tank mixing with phenoxy herbicides.
(Gaskin & Woon (1994) Weed Research 34:437-444)
Concentration (g)
2.5
2
1.5
1
0.5
0
Haloxyfop ester @50gai/ha
Plus 2,4-D butyl @ 500gai/ha
Plus 2,4-D butyl @ 1500gai/ha
Plus 2,4-D DMA @ 500gai/ha
Plus 2,4-D DMA @ 1500gai/ha
Plus MCPA butyl @ 500gai/ha
Plus MCPA butyl @ 1500gai/ha
Plus MCPA K salt @ 500gai/ha
Plus MCPA K salt @ 1500gai/ha
Root
Shoot
ICAN

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Group 1(A)
ACCase inhibitors

Tank mixing

Phenoxies (2,4-D, MCPA)

- Amines may reduce leaf uptake
- Amines and esters = faster metabolism within the plant
  => Less herbicide reaches the crown of the plant

Soybean post-ems e.g. Basagran® / Blazer®

- Oil required for Verdict® / Select® increases uptake
  => more crop damage from the broadleaf herbicide
- **Speed of activity (esp Blazer®) limits Verdict® / Select® translocation**

Timing

- Split applications
  - Minimum of 5 days (10 is better)

45

Group 1(A)
ACCase inhibitors

Application

For best results

- Good spray coverage (> 80L/ha. Medium to medium/coarse)
- Small weeds (up to early tillering)
- Conditions favouring good translocation
  - Avoid cold/frosty conditions; moisture stress; water logging
- Use the right adjuvant(s) (COC/wetter)
- Clethodim can disassociate in high bicarbonate water. AMS may help.
- Avoid mixing with broadleaf herbicides

Residues in grain

- No application once crop commences flowering
- Label rates

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Group 1(A)
ACCase inhibitors

Resistance

Ryegrass = widespread nationally

Feathertop Rhodes, Barnyard grass, Liverseed = confirmed & emerging (broadacre)

Crowsfoot = recently confirmed (soybeans in Burdekin)

- Target-site resistance
  - Test – Different target site substitutions affect different herbicides
- Metabolic resistance
  - Cross-resistance
  - Dose responsive?

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Group 1(A)
ACCase inhibitors

Resistance

			Group 1(A)					
		Tested	No. resistant	Clodinafop (Topik®)	Propaquizafop (Shogun®)	Haloxyfop (Verdict®)	Clethodim (Select®)	glyphosate
Cotton survey 2019	Feathertop	12	2	R	R	S	S	
	Barnyard	8	1	R	R	S	S	
			1	S	R	S	S	
	Liverseed	1	1	R	S	R	S	
Broadacre grains survey 2019	Feathertop	62	1	NT	NT	R	S	68%
	Barnyard	42		NT	S	NT	S	36%
	Windmill	12		NT	S	NT	S	58%
	Liverseed	3		NT	S	NT	S	0%
Soybean (Burdekin 2021)	Crowsfoot	3	2	NT	NT	R	NT	

R = resistant S = susceptible NT = not tested

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Group 2(B)

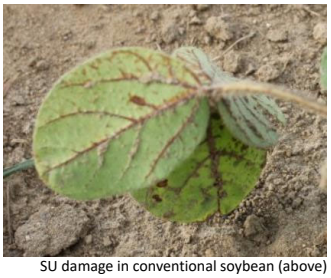
SU - Sempra® (halosulfuron-methyl)

IMI - Raptor® (imazamox), Spinnaker® (imazethapyr), Lightning® (imazethapyr/imazapyr), Flame® (imazapic)

TPS - BroadStrike® (flumetsulam)

Inhibits acetolactate synthase (ALS)

- Key enzyme in production of the amino acids leucine and valine (plus other compounds)
- ALS occurs throughout the plant, mainly in the chloroplasts
- Most active in meristematic regions - more active on young weeds where cell growth is a primary activity



SU damage in conventional soybean (above)
BroadStrike applied post-em (below)

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Group 2(B)
ALS inhibitors

Leaf entry & translocation

Intermediate lipophilicity

- Moderate to quick speed of leaf entry

Adjuvants – follow label advice for post-em use

- Spray oil (COC) may increase penetration = increased crop effect

Translocates rapidly in both xylem & phloem

- Plant growth inhibited within hours; days for symptoms to appear
- Needs active growth for phloem movement (i.e. not stressed)

Target small, actively growing weeds

50

Group 2(B)
ALS inhibitors

Soil activity

Easily washed off stubble / trash.

Mobile in the soil
- Horizontal movement into planting furrow
- Leaching

Soil persistence varies
- Sempra®, Raptor® = short to moderate
- BroadStrike®, Spinnaker®, Lightning® = moderate to long
- Flame® = very long
  - Carry-over from cane

Soil type
- IMIs persist longer in acid soils
- SUs persist longer (and more available) in alkaline soils

Intervix® in sorghum (Trevor Philp)

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Group 2(B)
ALS inhibitors

Crop selectivity

Conventional crops (e.g. Spinnaker® in soybeans)
- Selectivity comes from rapid herbicide metabolism
  - Crops under stress will show more symptoms

Herbicide tolerant crops
- HB1 soybeans (New Bunya HB1(ϕ), Mossman HB1(ϕ), Kuranda HB1(ϕ))
  - Tolerance to Sempra® via target site substitution (Pro178Ser)
- Clearfield® maize
  - Tolerance to IMIs via target site substitution (Ser-653-Asn)

Spinnaker® damage in soybeans (QDAF)

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Group 2(B)
ALS inhibitors

Resistance

Target-site resistance is very common – especially for SU's

- 26 different substitutions @ 7 locations are currently known
- Field failures in as little as 4 selections
- Cross-resistance between Group 2(B) sub-groups depends on the mutation selected

Metabolic resistance may also occur

- Typically low order, and may not be noticed in populations with target-site resistance

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Group 2(B)
ALS inhibitors

Known interactions

Sulfonylurea group – don't acidify the spray tank

- Solubility decreases under acidic conditions
  - e.g. Sempra® 1630 mg/L @ pH 7, 15 mg/L @ pH 5
- Hydrolysis (degradation) at pH < ~5

Krismat® + Li700

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Group 2(B)
ALS inhibitors

Known interactions

Spray tank residues – particularly sulfonylurea group (e.g. Sempra®)

Rinsing with water inadequate if moving to a sensitive crop

- Triple rinse with water
- Then disassemble & clean filters, nozzle bodies etc.
  - Pay special attention to dead end areas e.g. end of boom, sumps etc.
- Then decontaminate with bleach or boom cleaner specifically labelled for sulfonylurea decontamination
  - Two decontaminations may be required

EC formulations (solvent) may 'strip out' SU residues

- e.g. Group 1(A) grass herbicides; chlorpyrifos; dimethoate

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Group 5/6(C)
PSII inhibitors

Photosystem II inhibitors (old Group C)

Group 5	
triazines	ametryn, atrazine, Terbyne® (terbuthylazine)
triazinones	Amitron® (amicarbazone), hexazinone, metribuzin
ureas	diuron

Group 6	
benzothiadiazinones	Basagran® (bentazone)
nitriles	Buctril® (bromoxynil)

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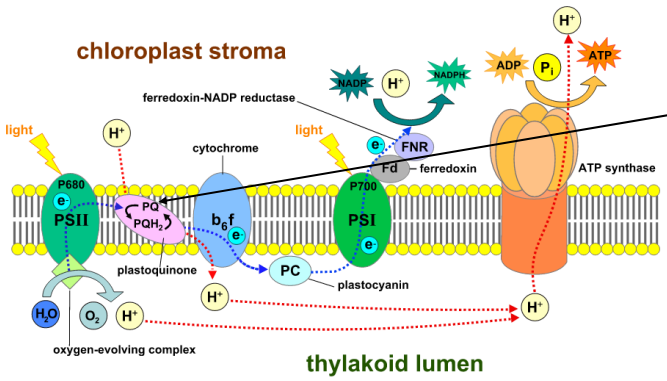
Group 5/6(C)
PSII inhibitors

Mode of action



Disrupts photosynthesis within the chloroplasts at Photosystem II

- Prevents plastoquinone binding
- Without plastoquinone accepting high-energy electrons, cell wall leakage occurs

Source: Somepics, CC BY-SA 4.0, https://commons.wikimedia.org/w/index.php?curid=38088695

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Group 5/6(C)
PSII inhibitors

Leaf uptake

Atrazine® / Terbyne® / diuron
- Moderately lipophilic
- Some / limited leaf uptake
- Respond strongly to oils & COCs

Amitron® / Velpar® / metribuzin
- Weakly to moderately lipophilic
- Some leaf uptake
- Non-ionic surfactant (or COC) preferred adjuvant

Root uptake from overspray onto soil important for these groups

Basagran®
- Neutral lipophilicity
- Better leaf uptake, but slow
  - 8 hour rainfast
- Non-ionic surfactant if needed.
  - Oils can increase crop injury.

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Group 5/6(C)
PSII inhibitors

Translocation

Movement from leaf entry

- All have poor / very poor phloem movement.
- Limited movement upwards / outwards from point of leaf entry.

Typically consider as a contact herbicide.

Ensure good coverage & very small weeds for foliar applications.

Movement in the xylem when entering via the roots

- Soil uptake from overspray is important
- Terbyne® / atrazine / diuron
  - Low solubility = good soil moisture required for root uptake
- Amitron® / Velpar®
  - High solubility. Soil moisture somewhat less important (better suited to wash through cane trash blanket)

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Group 5/6(C)
PSII inhibitors

Crop tolerance

Relies on rapid metabolism

More crop effect:

- Plants under stress
- Adjuvants that increase rate of uptake
- Partner herbicide (adjuvants)

NSW DPI

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Group 5/6(C)
PSII inhibitors

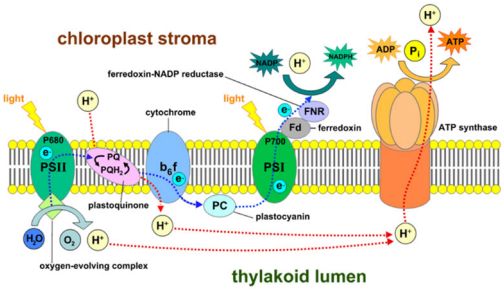
Known herbicide interactions

Group 17(H) herbicides (HPPD inhibitors) block synthesis of plastoquinone (PQ)

- Reduced levels of PQ = less competition with Group C herbicides at the Q_B binding site

PS II herbicides block PQ transferring electrons to PS I

- Paraquat requires these electrons for activity
- May reduce/slow the performance of paraquat.



61

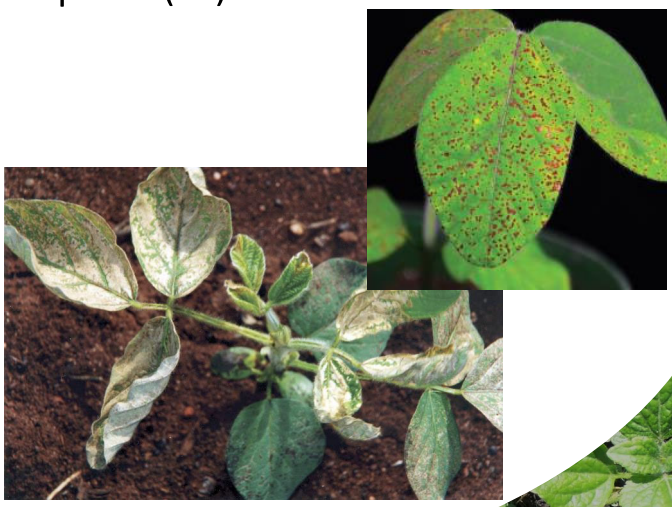
Group 14(G)

Blazer® (acifluorfen)

- soybean pre & early–post

Valor® (flumioxazin)

- Soybean pre-em only
- Cane
- Fallow

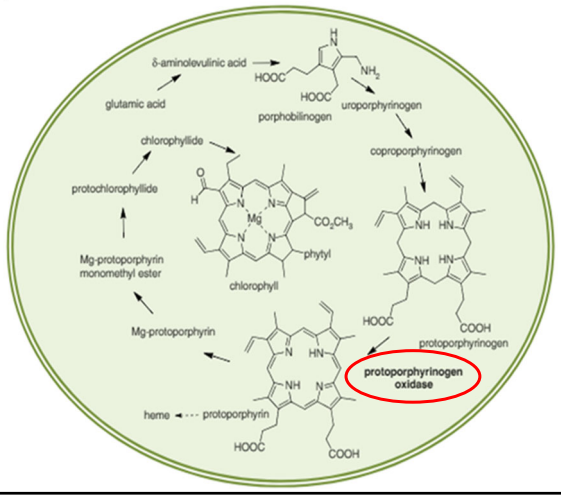


Blazer (QDAF)

62

Group 14(G)
PPO inhibitors

Mode of action



Inhibits protoporphyrinogen oxidase (PPO)

- Protoporphyrinogen then leaks into the cytoplasm where oxidation to protoporphyrin is unregulated
- Triplet state protoporphyrin and singlet oxygen are formed, extracting hydrogen from unsaturated lipids and proteins
- **Results in leaky cell membranes, loss of heme and chlorophyll production**

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Group 14(G)
PPO inhibitors

Leaf entry

Moderately lipophilic = relatively fast leaf entry

Adjuvants increase uptake (in both weeds and crop)

- No adjuvant < non-ionic surfactant < COC
- Also consider adjuvant from other tank mix partners

64

Group 14(G)
PPO inhibitors

Speed of activity

Foliar activity is fast-acting, especially under high light intensity

- Limited / no translocation. Contact herbicides.
  - Sharpen® (saflufenacil) has best chemical properties for translocation
- Weed size must be small
  - Much easier to hit the growing point of broadleaf weeds
  - Good coverage is required (80L+ / ha. Medium spray quality)

Crop selectivity (Blazer®)

- Relies on rapid metabolism (in soybean) and poor translocation
- Will burn crop foliage, but new growth unaffected.
- High light intensity / high rate / adjuvants increase activity
  - both crop and weeds

65

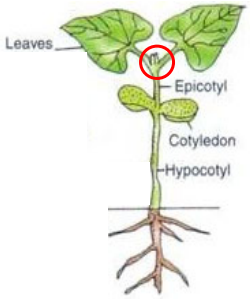
Group 14(G)
PPO inhibitors

Spectrum of activity

Strongest on small, broadleaf weeds post-em

At higher application rates (i.e. ~ 2 – 5 X)

- Several (but not all) Group 14s provide residual activity
- Many also provide some grass weed activity at these application rates



66

Group 14(G)
PPO inhibitors

Known herbicide interactions

Fast speed of activity (1-2 days)

- Destroys vascular tissue => reduced opportunity for translocation

Avoid mixtures with herbicides that take time to translocate

- Group 1(A)
  - Oil required for the Group 1(A) will 'hot up' Blazer® on the crop
  - Speed of activity of Blazer® will reduce Group 1(A) translocation
- Glyphosate (especially in summer)

67

Group 4(I)

2,4-D drift (QDAF)

Fluroxypyr drift

(QDAF)

Picloram drift/residues

68

Group 4(I)
Auxin mimics

Group 4(I)

Arylpicolinates	halauxifen (Arylex®)
Benzoic acids	dicamba
Phenoxy's	2,4-D, MCPA
Pyridines	aminopyralid, clopyralid, fluroxypyr, picloram, triclopyr

- Auxin herbicides mimic indol-3-acetic acid (IAA)
- IAA
  - Responsible for cell division, differentiation and elongation
  - Controls seedling morphology, apical dominance, leaf senescence and other whole-plant process, plus abscission, flowering and fruit production.
  - Regulated by ethylene production
- Auxin binding proteins
  - Cell membrane, endoplasmic reticulum, cell nucleus and cytoplasm

69

Group 4(I)
Auxin mimics

Leaf uptake

Active via foliar uptake.
- Soil uptake varies with product and application rate.

Applied as esters or salts (amines)
- Leaf uptake of esters (e.g. 2,4-D, fluroxypyr) is faster
- Amines (2,4-D, dicamba, picloram) is slower (hours)
  - Less rainfast
  - Surfactants more important

Both ester and amine converted to herbicidally active parent acid once inside the leaf

70

Group 4(I)
Auxin mimics

Translocation & selectivity

Relatively fast to move throughout the plant

- Well transported in the xylem & phloem
- Auxin binding receptors and ion-trapping aid cell entry

Selectivity

- Conversion to the acid
- Translocation
- Metabolism

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Group 4(I)
Auxin mimics

2,4-D application

Volatility

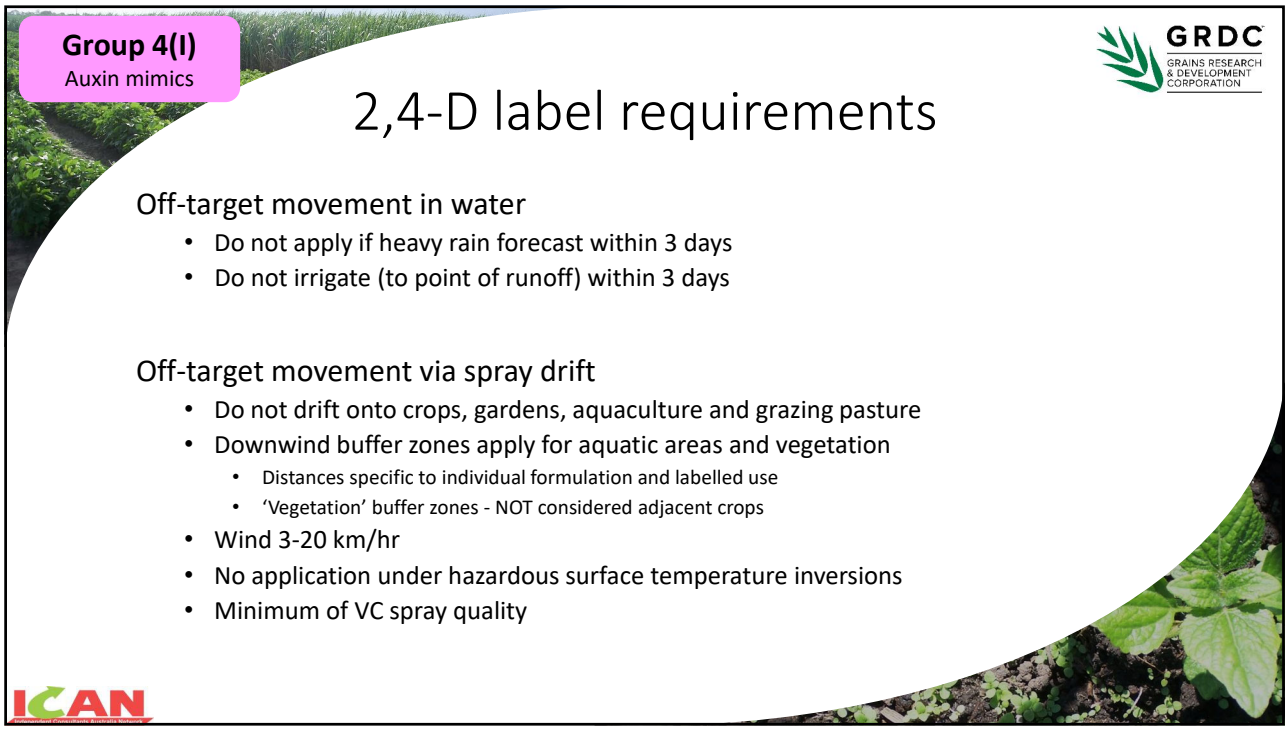
- Very small difference between amines and current ester (2-ethylhexyl)

Drift

- **Droplet size (nozzle selection)**
- Boom height / travel speed / wind
- Adjuvant
  - In the formulation
  - Tank mixed

- Good translocation = able to apply as large droplets
  - Reduces drift
  - Efficacy maintained, depending on water rate
    - 50+L/ha for 'larger' weeds. Need 80-100 L/ha if weeds are very small

72


Group 4(I)
Auxin mimics
GRDC
GRAINS RESEARCH & DEVELOPMENT CORPORATION
2,4-D label requirements
Off-target movement in water
• Do not apply if heavy rain forecast within 3 days
• Do not irrigate (to point of runoff) within 3 days
Off-target movement via spray drift
• Do not drift onto crops, gardens, aquaculture and grazing pasture
• Downwind buffer zones apply for aquatic areas and vegetation
• Distances specific to individual formulation and labelled use
• 'Vegetation' buffer zones - NOT considered adjacent crops
• Wind 3-20 km/hr
• No application under hazardous surface temperature inversions
• Minimum of VC spray quality
ICAN

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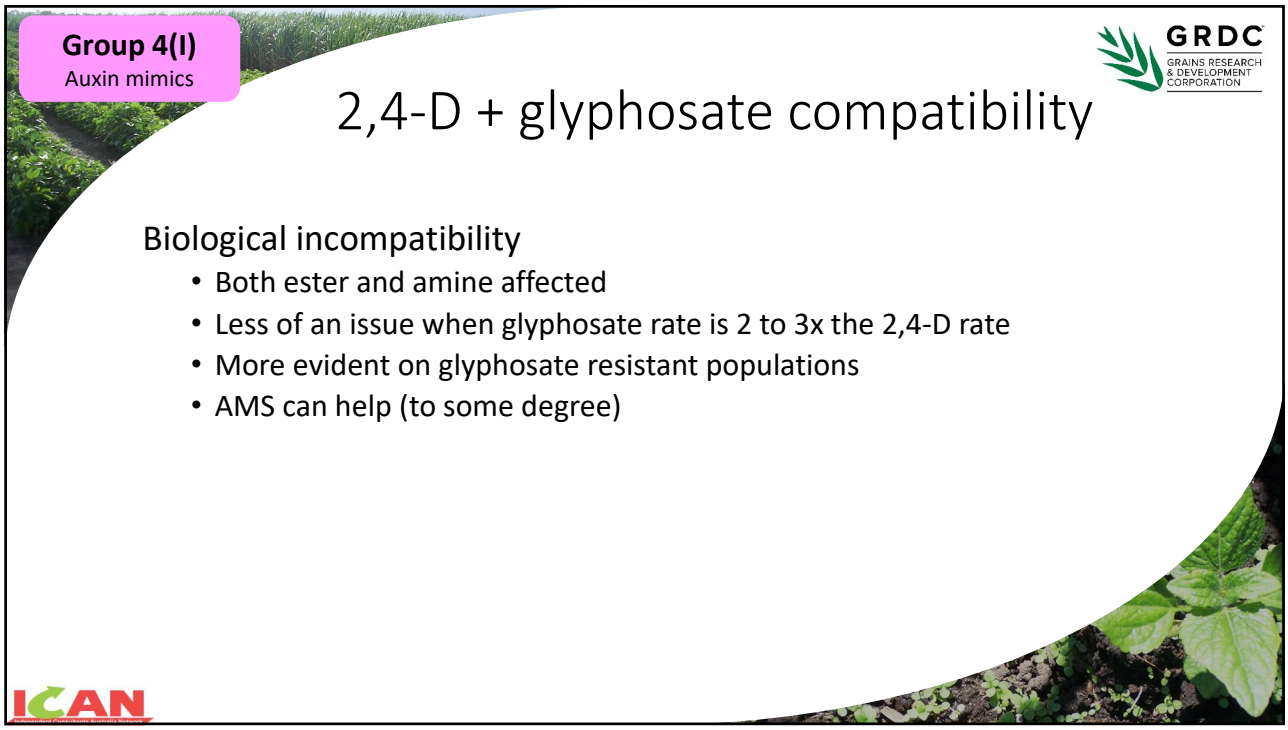
Group 4(I)
Auxin mimics
GRDC
GRAINS RESEARCH & DEVELOPMENT CORPORATION
2,4-D + glyphosate compatibility
Biological incompatibility
• Both ester and amine affected
• Less of an issue when glyphosate rate is 2 to 3x the 2,4-D rate
• More evident on glyphosate resistant populations
• AMS can help (to some degree)
ICAN

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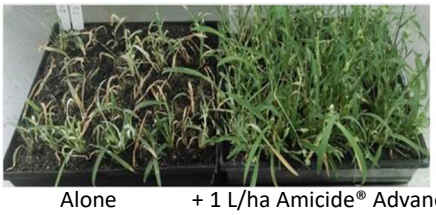
Group 4(I)
Auxin mimics

Biological antagonism with glyphosate

0.5 L/ha Roundup® PowerMax



Alone + 1 L/ha Amicide® Advance

Alone + 1.03 L/ha Estercide® Xtra 680

1 L/ha Roundup® PowerMax

Alone + 1 L/ha Amicide® Advance

Alone + 1.03 L/ha Estercide® Xtra 680

Low-level (2x) target site resistant annual barnyard grass population

https://ahri.uwa.edu.au/24-d-antagonises-glyphosate-especially-in-glyphosate-resistant-weeds/

75

Group 4(I)
Auxin mimics

2,4-D + glyphosate compatibility

Physical compatibility in the spray tank

- 2,4-D amine is more problematic
- Use matched salts where possible
- Mixing order is important
  - Water => AMS => 2,4-D => glyphosate => surfactant
- Water
  - Address water issues (hardness & bicarbonate)
  - Cold water will be worse
  - Keep water rates up
  - Keep pH > 5 to 5.5

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Group 22(L)

e.g. Gramoxone® (paraquat); Spray.Seed® (paraquat + diquat)

Paraquat drift (QDAF)

(NSW DPI)

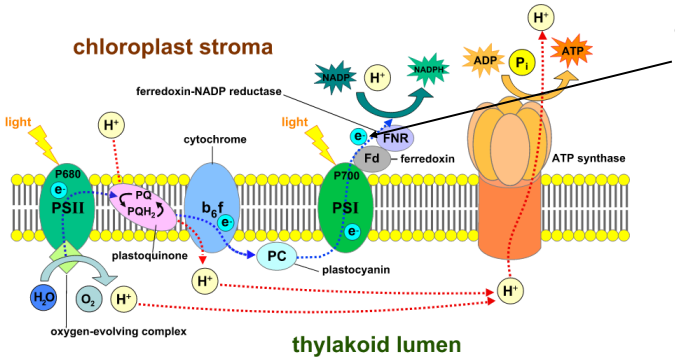
77

Group 22(L)
PSI disruption

Mode of action

Disrupts photosynthesis within the chloroplasts at Photosystem I

- Paraquat (PQT^{++}) hijacks PSI electrons and is reduced to a PQT^{+} free radical.



Source: Somepics, CC BY-SA 4.0, https://commons.wikimedia.org/w/index.php?curid=38088695

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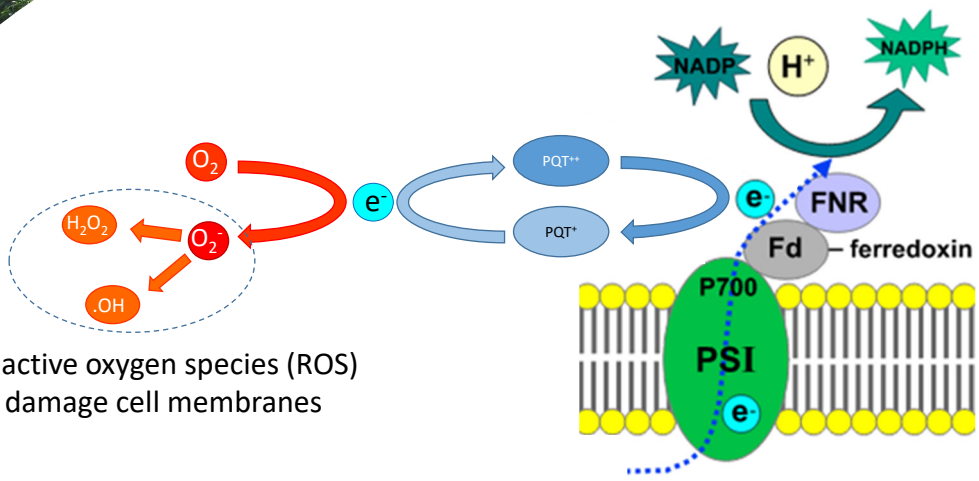
Group 22(L)
PSI disruption

Mode of action



Reactive oxygen species (ROS) damage cell membranes

79

Group 22(L)
PSI disruption

Leaf entry

Positively charged (but hydrophilic)
- Very rapid cuticle penetration
- Rainfast within minutes

Surfactant is important
- Gramoxone® 360 Pro does not contain surfactant
- 250g/L formulations
  - Rates less than 1L / 100L may benefit from added non-ionic surfactant
- Oil and AMS doesn't help paraquat

Binds extremely tightly to soil colloids & organic matter.
- Use clean water

80

Group 22(L)
PSI disruption

Translocation

Some movement in the apoplast (between cells)

Limited mobility in vascular tissue
- Any movement that occurs outside of the treated leaf is in the xylem
- Rapid cell membrane damage destroys the vascular bundle

Contact herbicide
- Ensure good coverage – water rate; surfactant

Activity requires light
- More hours to move if applied in the dark

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Group 22(L)
PSI disruption

Water rates

Summer rainfall areas	Boom spray volumes
Small plants (2-5 leaf) and well separated	50-100L/ha
5 leaf to early tillering/rosettes; 30-50% ground cover	100-150L/ha
Advanced growth; dense and/or tall weed growth	150-200L/ha
Very dense and tall weed growth	Use a split application @ 150L/ha to remove excessive growth

Spray.Seed® Herbicide label.
Similar recommendations would apply to paraquat herbicides.

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Group 22(L)
PSI disruption

Metabolism

Not metabolised in the plant

- May be released from cell upon cell wall rupture & move to next cell
- Eventually gets trapped in dead cell material & won't move any further

=> application coverage is essential

83

Group 22(L)
PSI disruption

Resistance

Vacuole sequestration only reported resistance mechanism

- Often 'low level' resistance in initial stages (rate creep)
- May be temperature dependent (species dependent)

Barley grass – widespread in long term lucerne paddocks throughout south eastern Australia
Brome grass & ryegrass – southern states
Fleabane – Hunter Valley
Tall fleabane – Darling Downs
Crowsfoot, blackberry nightshade, cudweed – Bundaberg

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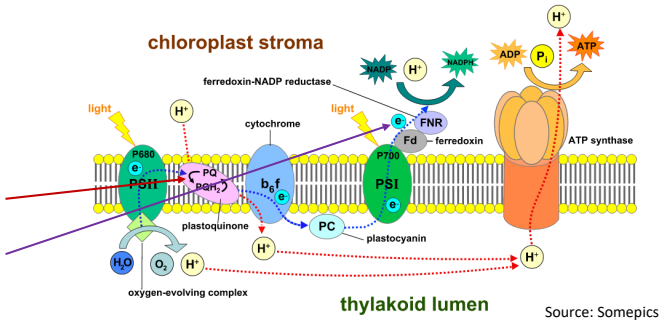
Group 22(L)
PSI disruption

Known interactions

Group 5 (e.g. diuron, atrazine)

Group 27 (e.g. Balance®)

- Both groups disrupt PQ at PSII, shutting down electron transfer (dark blue line)
- Therefore reduced electron availability at PSI



Source: Somepics

Theory: slows down speed of paraquat activity = more time to translocate = better weed control
Practice: don't always see benefit in the paddock

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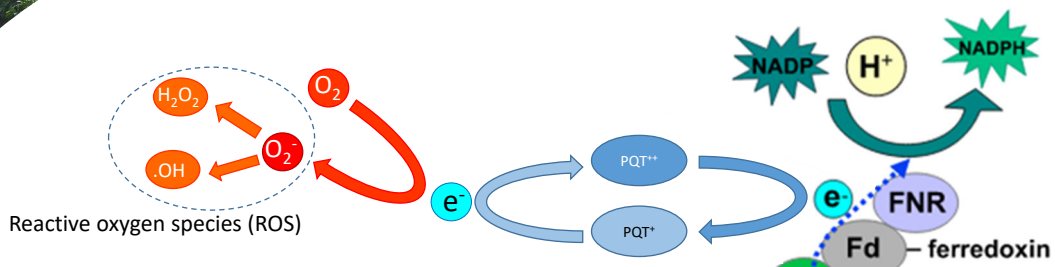
Group 22(L)
PSI disruption

Known interactions



Reactive oxygen species (ROS)

Paraquat creates additional reactive oxygen (ROS) => cell membrane damage

Carotenoids = cell defence against ROS

Amitrole (Group 34) blocks production of carotenoids, so mixes with amitrole may improve weed control
(e.g. Alliance, Para-Trooper®, Guerrilla®)

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Group 9(M) glyphosate

(QDAF)

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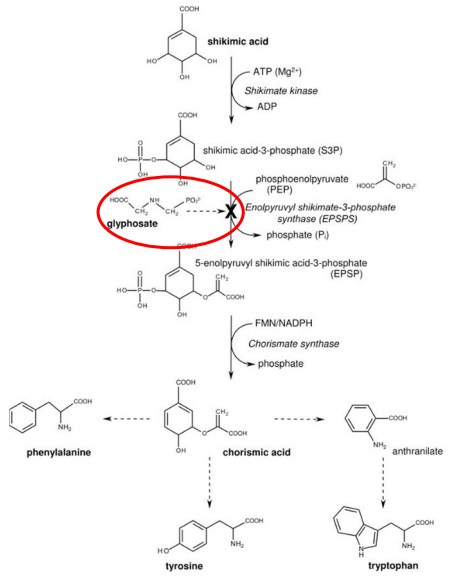
Group 9(M)
EPSPS inhibition

Mode of action



Inhibits 5-enolpyruvyl-shikimate-3-phosphate synthase (EPSPS)

- Blocks production of 3 key aromatic amino acids (phenylalanine, tyrosine and tryptophan)
- Reduces other secondary products required to fix carbon for plant growth

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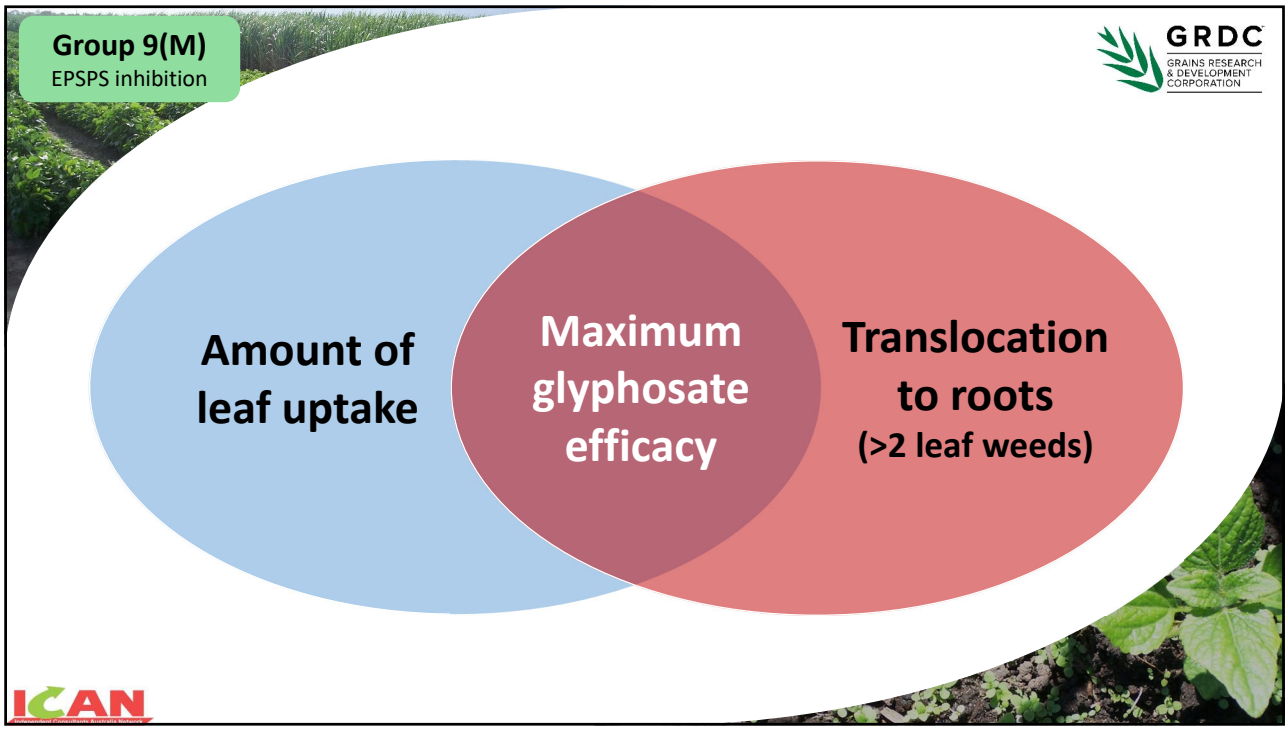
Group 9(M)
EPSPS inhibition
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Amount of leaf uptake
Maximum glyphosate efficacy
Translocation to roots
(>2 leaf weeds)
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Group 9(M)
EPSPS inhibition
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Leaf entry
Time (hours) for leaf entry depends on:
• Climatic conditions (condition of the leaf cuticle; rate of moisture evaporation)
• Droplet size (rate of moisture evaporation)
• Formulation (rate of moisture evaporation; rate of penetration)
• Adjuvant (amount of spread; rate of penetration)
• Application rate
• Antagonism in the spray tank (water quality; other pesticides)
Small weeds + mild conditions + robust rate + no resistance
=> Unlikely to see differences from formulation / adjuvant / spray setup
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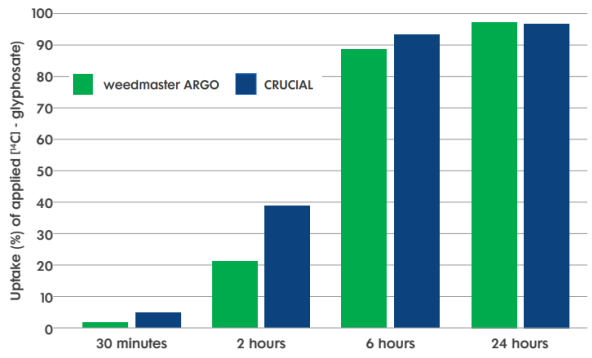
EPSPS inhibition

Speed of uptake

- Formulated as a salt (amine)
- Difficult to penetrate the cuticle
  - esp. feathertop Rhodes grass, crowsfoot, fleabane
- Slow uptake = relatively poor rainfastness



Nufarm Crucial® Techguide August 2021 (weed = ryegrass)

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Group 9(M)
EPSPS inhibition

Temperature

Under 'hot & low humidity' conditions

- Less moisture in the leaf cuticle reduces leaf uptake
- Reduced translocation to the roots
- Increasing application rate may help. Preferably wait 'a few days' after heat wave.

Effect of temperature on efficacy of (glyphosate susceptible) barnyard grass

	Rate required (gae/ha) for		
	50% control	**100% control**	
Warm 20/25ºC	65	112	
Hot 30/35ºC	170	>337	337g/ha was the highest rate tested which only gave 90% control

Adapted from Target-site EPSPS Pro-106 mutations: sufficient to endow glyphosate resistance in polyploid Echinochloa colona? (Han, Yu, Widderick, & Powles. 2015)

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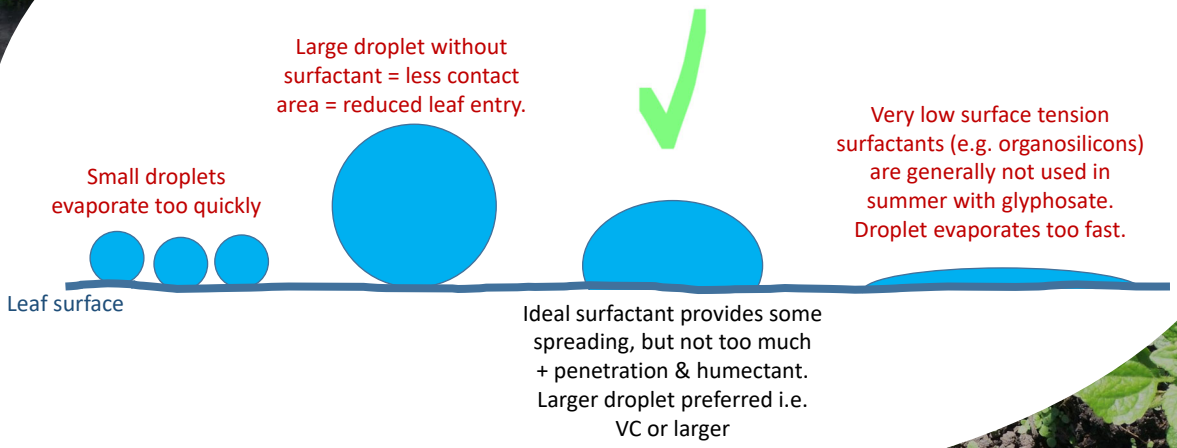
EPSPS inhibition

Droplet size & spread

Large droplets with minimal spread under 'hot & low humidity' conditions



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Group 9(M)
EPSPS inhibition

Surfactant

Additional tank-mixed surfactant for glyphosate?

- Inadequate surfactant in the formulation. (But how do you know?)
- Glyphosate rate is low (i.e. < 1L/ha) and spray volume high i.e. > 200L/ha
- High level of leaf spread / coverage is required e.g. woody weed applications
- Partner herbicide requires a specific surfactant
  - But beware that this may negatively affect glyphosate performance

Don't use organosilicates e.g. Pulse® for summer broadacre applications

Crop-oil-concentrates e.g. Uptake®, Hasten® etc.

- Glyphosate is water-loving – so won't benefit from an 'oil'
- 15-25% surfactant in COCs may increase droplet spread
- COCs may **reduce** glyphosate performance on summer grasses

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Similar to original Roundup CT formulation

- 120-150 g/L tallow amine (15) surfactant
- Tallow amine is an eye irritant and moderately toxic. So now requires labelling.
- Also likely to contain polyethylene glycol (PEG)
  - Reduced formulation viscosity
  - Humectant = reduced droplet evaporation

Tallow amine (and PEG)

- Not used in high load CT formulations
- Not used in any formulation for aquatic use
- Unlikely to be used in
  - 'Fully loaded' formulations
  - Dual/triple salt formulations

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EPSPS inhibition

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Surfactant load

Target active load of around 150-200 gai/100L (**0.15 to 0.2 %**) for surfactants

Research trials show advantages of additional surfactant

Glyphosate 450 CT containing		Spray volume				
		50 L/ha	75 L/ha	100 L/ha	150 L/ha	200 L/ha
120g/L polyethanoxy (15) tallow amine surfactant	0.5L/ha	0.12	0.08	0.06	0.04	0.03
	1 L/ha	0.24	0.16	0.12	0.08	0.06
	2L/ha	0.48	0.32	0.24	0.16	0.12
144g/L polyethanoxy (15) tallow amine surfactant	0.5L/ha			0.07	0.05	0.04
	1 L/ha	0.29	0.19	0.14	0.10	0.07
	2L/ha	0.58	0.38	0.29	0.19	0.14

Common grower use rates

Inadequate	Marginal	Optimal	Excess

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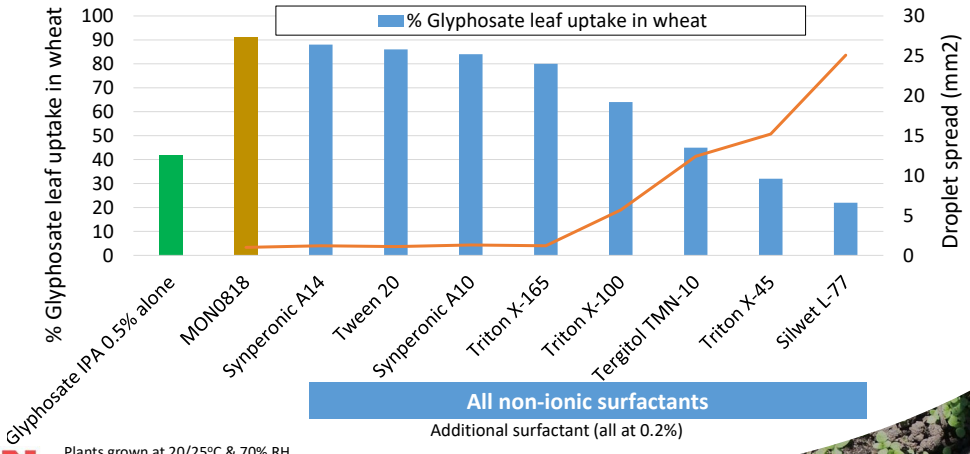
EPSPS inhibition

Surfactant type

Best adjuvant for glyphosate IPA for 'tough' jobs

- Tallow amine (15) ethoxylate e.g. Glysowet Surfactant (SST); GlyWetter Plus (Rygel)



Plants grown at 20/25°C & 70% RH
Adapted from Liu. Z.Q. (2003) Characterization of glyphosate uptake into grass species.

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Group 9(M)
EPSPS inhibition

Water quality

Water quality – Glyphosate binds tightly to soil colloids & organic matter.

- Dust / wheel tracks.
- Use clean water.

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Group 9(M)
EPSPS inhibition

Water quality

Water quality - pH

- Spray tank pH ~4.5 to 5.6 <u>after</u> glyphosate added

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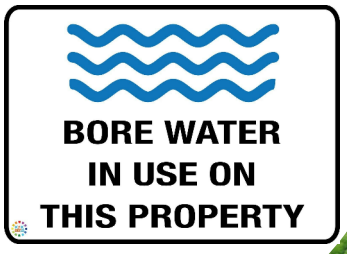
Group 9(M)
EPSPS inhibition

Water quality

Water quality

Polyvalent cations (total hardness)

- (Ca^{++}, Mg^{++}, Na^{++}, K^{++}, Fe^{++}, Fe^{+++}, Al^{+++}) antagonise glyphosate
- Calcium is a common cause of water hardness
  - Glyphosate salt dissociates and preferentially forms Gly-Ca salt
- Total hardness
  - 200ppm = concern; 400ppm+ = problem
- Watch foliar fertiliser tank mixes



Bicarbonates (total alkalinity)

- May not be reported on standard water test
- 75ppm = concern; 150ppm = problem
- Particularly damaging to phenoxy amines & DIMs
- Can also affect glyphosate and other salt formulations

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Group 9(M)
EPSPS inhibition

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Ammonium sulphate (AMS)

Glyphosate's favourite 'wing man'

- 'Fixes' hard water
- Partially fixes high bicarbonates
- Helps with tank mix compatibility
- Assists cell membrane transfer

But needs time

- Fully dissolve in spray tank
  - If impatient – use a liquid formation
- Further 5-10 minutes under agitation

Kg ammonium sulphate /100 L = (0.001 x Ca (ppm)) + (0.0006 x Na) + (0.0002 x K) + (0.0017 x Mg)

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EPSPS inhibition

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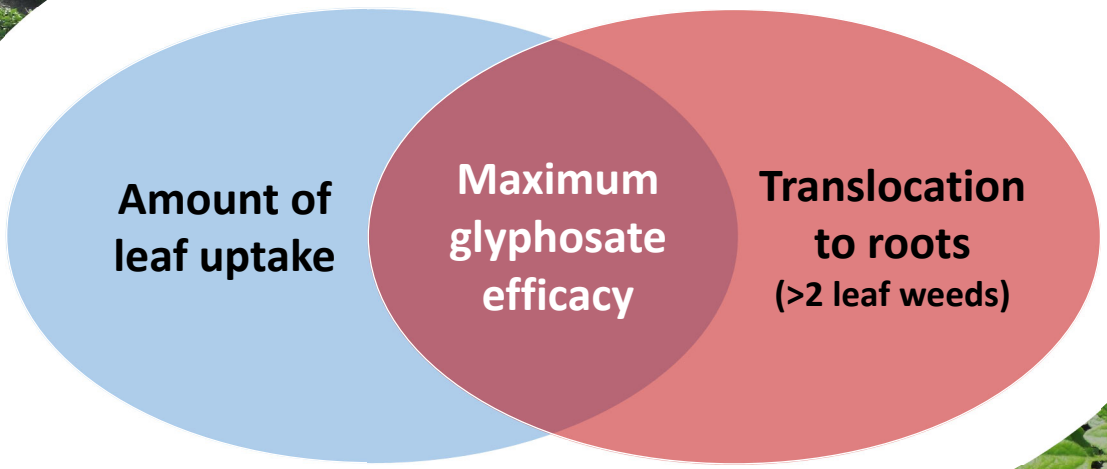

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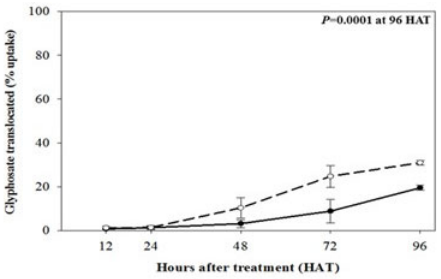
Group 9(M)
EPSPS inhibition

Translocation

- Good soil moisture.
- Target actively growing small weeds
- ~ 30-50% 'trapped' in leaf where it entered
- Useful upwards & outwards movement in the apoplast and xylem
- Mobility in the phloem is very important
  - Only commences from 2nd true leaf
  - Transported with sugars
  - Self limiting. ~3 days, sugar production is declining

  => Allow minimum of 3 days for annual weeds before double knocking or cultivation for optimum uptake

Translocation of C^{14} glyphosate to roots of *Lolium rigidum*.
Dash line = susceptible population
Solid line = resistant population



Fernandez-Moreno et. al. (2017) Evidence, mechanism and alternative chemical seedbank-level control of glyphosate resistance of a rigid ryegrass (*Lolium rigidum*) biotype from southern Spain.

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Group 9(M)
EPSPS inhibition

Speed of brownout

'Fast acting' partner herbicides that damage vascular bundle reduces glyphosate translocation to the roots

- e.g. paraquat / Group 14 (G) / glufosinate
- The faster this happens, the more glyphosate translocation will be impacted

Photo Matt Witney

Tank mixing seeking 'fast brownout' is **NOT** a desired feature for glyphosate.

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Group 9(M)
EPSPS inhibition

Partner herbicide incompatibility

	Physical	Biological
Group 1(A)		Sometimes evident
SUs		If spray tank pH drops too low i.e. <5
Group 5(C)	Particularly clay based formulations	
trifluralin	Under certain conditions/formulations*	
propyzamide	Under certain conditions/formulations*	
Group 14(G)	May add to other problems	**Weak to strong. Depends on herbicide, rate, climatic conditions**
2,4-D	Under certain conditions/formulations* **More likely with amine formulations**	Generally weak to moderate
dicamba		Low pH increases dicamba volatility
paraquat		**Strong**
glufosinate		**Moderate to strong**
Oil adjuvants		Depends on formulation & weed species (esp. BYG)

* Single K salt formulations are generally more problematic

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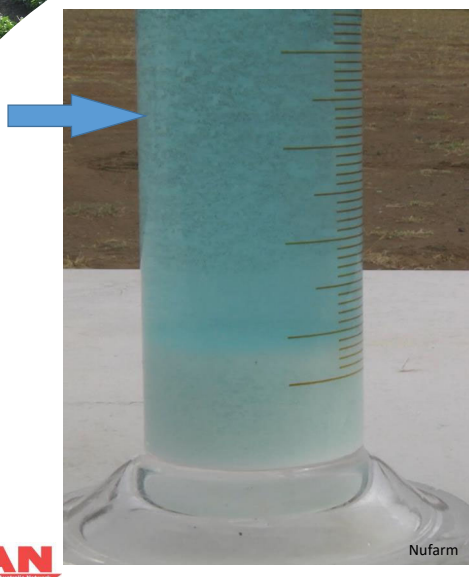
Group 9(M)
EPSPS inhibition

Glyphosate + 2,4-D amine



Considerations for tank mixing

- Unmatched salts
  - esp. glyphosate K salt + 2,4-D DMA salt
- Water
  - Hard water
  - Cold water
  - Acidic pH
  - Low water volume
- Ratio of glyphosate to 2,4-D
  - At least 2:1
- Mixing sequence

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Group 9(M)
EPSPS inhibition

Resistance

Target site substitution
- Ryegrass, barnyard grass, feathertop Rhodes grass

Gene amplification
- Brome grass, windmill grass

Vacuole sequestration
- Ryegrass, fleabane
- Increases with higher temperatures

Enhanced metabolism
- Barnyard grass

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Group 9(M)
EPSPS inhibition

Resistance

Effect of temperature on efficacy of barnyard grass

		Rate required (gae/ha) for		
		50% control	100% control	
Susceptible	**Warm 20/25°C**	65	112	
	Hot 30/35°C	170	>337	337g/ha was the highest rate tested which only gave 90% control
Resistant (3.3X)	**Warm 20/25°C**	216	337	
	Hot 30/35°C	539	>900	900g/ha was the highest rate tested which only gave 90% control

Adapted from Target-site EPSPS Pro-106 mutations: sufficient to endow glyphosate resistance in polyploid Echinochloa colona? (Han, Yu, Widderick, & Powles. 2015)

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Group 9(M)
EPSPS inhibition

Resistance

Best chance of achieving control

- ✓Mild / warm (not hot & dry) temperature
- ✓Quality formulation (adjuvant package)
- ✓Large (VC) droplets
- ✓Small weeds
- ✓No rain for >6 hours
- ✓Robust application rates
- ✓Minimum water rate (that still achieves coverage)
- ✓AMS
- ✓Good water quality
- ✓No antagonistic adjuvants or partners

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Group 9(M)
EPSPS inhibition

Glyphosate: Double knock

Delay resistance + Improves efficacy

Second knock may be better timing for some tank-mix partners

- Fast-acting, non-systemics e.g. Group 14(G)
- Some pre-emergents

Timing of second knock

- Not before 3 days (glyphosate is still translocating)
- Grasses – optimal 4 to 7 days
- Broadleafs – optimal 7 to 14 days

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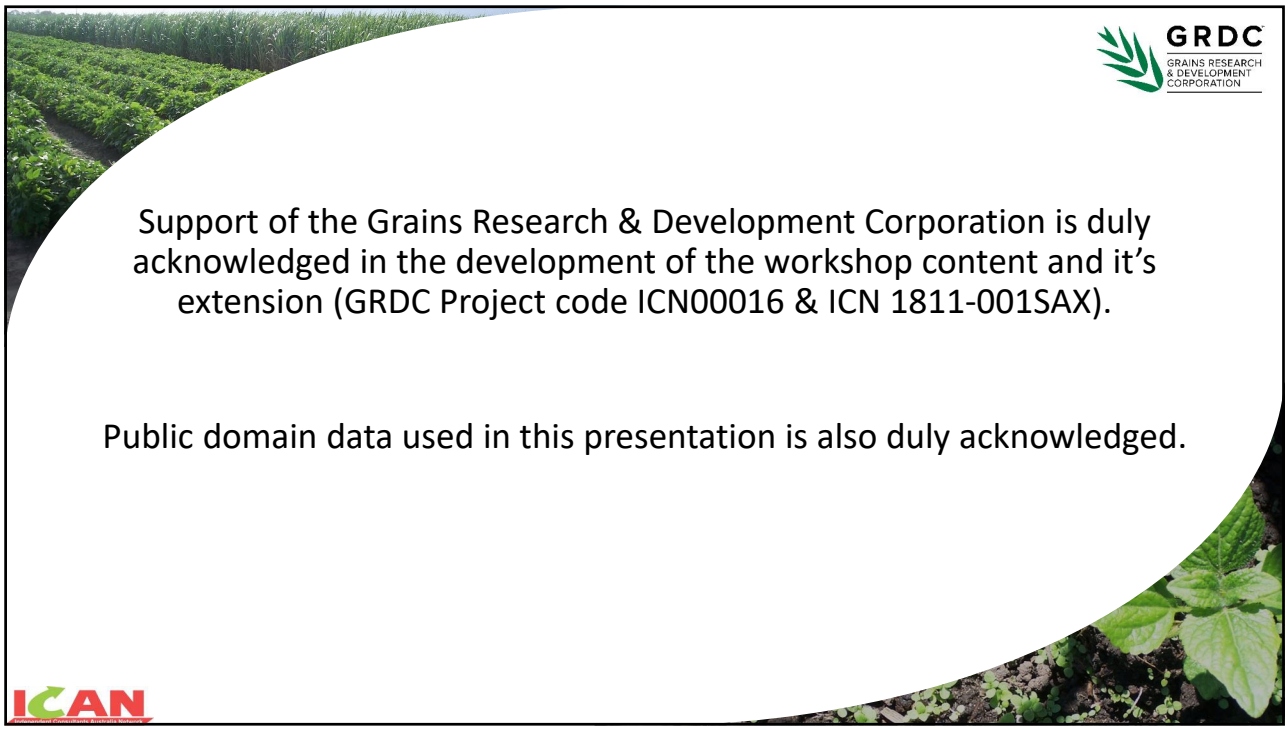
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Support of the Grains Research & Development Corporation is duly acknowledged in the development of the workshop content and it's extension (GRDC Project code ICN00016 & ICN 1811-001SAX).
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