Herbicide Mode of Action and Herbicide Resistant Weeds

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Objectives for this morning…

- Working definition of herbicide mode of action
  - and why it is important
  - resistance management
  - resources to help with problem solving

- Review of common modes of action
  - chemical families
    - used in many sites/crops common to Oregon
  - plant herbicide symptomology examples

Effective Chemical Weed Management

Herbicide application and placement

Herbicide uptake

Herbicide translocation

- movement within the plant through xylem and phloem tissue

Herbicide toxicity and activity

Herbicide metabolism and degradation

Mode of Action-Definitions

-Sequence of events from herbicide absorption to plant death

-Mechanisms by which a herbicide causes plant death

-The suite of plant process interfered with by a herbicide at the tissue or cellular level

-How a herbicide kills a plant

Site of Action

-Place in the plant where the herbicide acts…

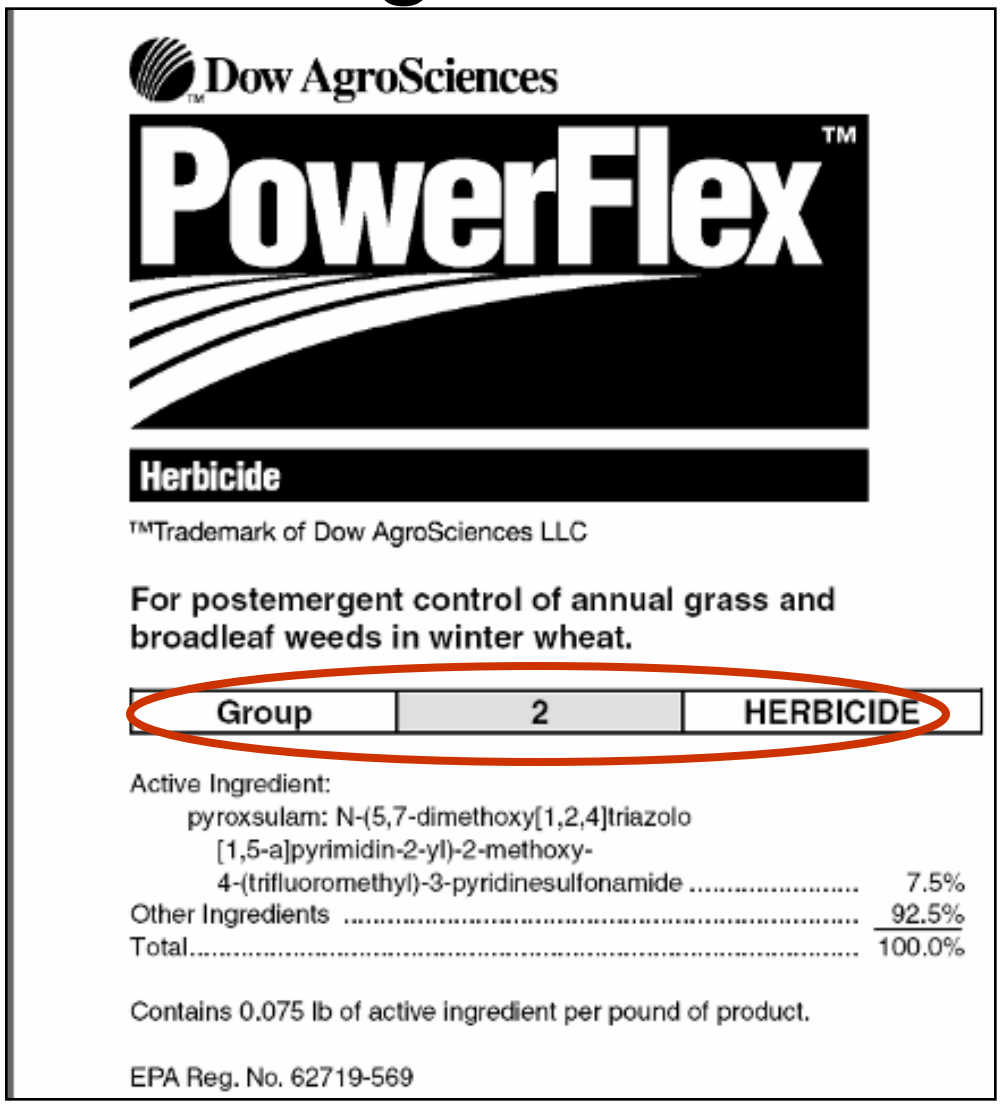
- specific mechanisms of action…

-Organized by “Groups”

-Group number usually printed on the label

Herbicide Classification for Resistance Management

- Herbicides are grouped by site of action
- Users are able to determine related chemistries
- EPA and Agriculture Canada are calling for voluntary labeling that would include group number



Dow AgroSciences

PowerFlex™

Herbicide

™Trademark of Dow AgroSciences LLC

For postemergent control of annual grass and broadleaf weeds in winter wheat.

Group	2	HERBICIDE

Active Ingredient:

pyroxsulam: N-(5,7-dimethoxy[1,2,4]triazolo [1,5-a]pyrimidin-2-yl)-2-methoxy-4-(trifluoromethyl)-3-pyridinesulfonamide 7.5%

Other Ingredients 92.5%

Total..... 100.0%

Contains 0.075 lb of active ingredient per pound of product.

EPA Reg. No. 62719-569

Herbicide-Resistant Weeds and Their Management

When planning a herbicide program to prevent resistance, do not use herbicides from the same group more than once within three years.

This publication contains the

Guide for Herbicide Rotation

reference poster

The authors—Carol Mallory-Smith, Professor of Weed Science, Oregon State University; Andy Hulting, Assistant Professor and Extension Weed Specialist, Oregon State University; Donn Thill, Professor of Weed Science, University of Idaho; Don Morishita, Professor of Weed Science, University of Idaho; Jen Krenz, Faculty Research Assistant, Oregon State University.

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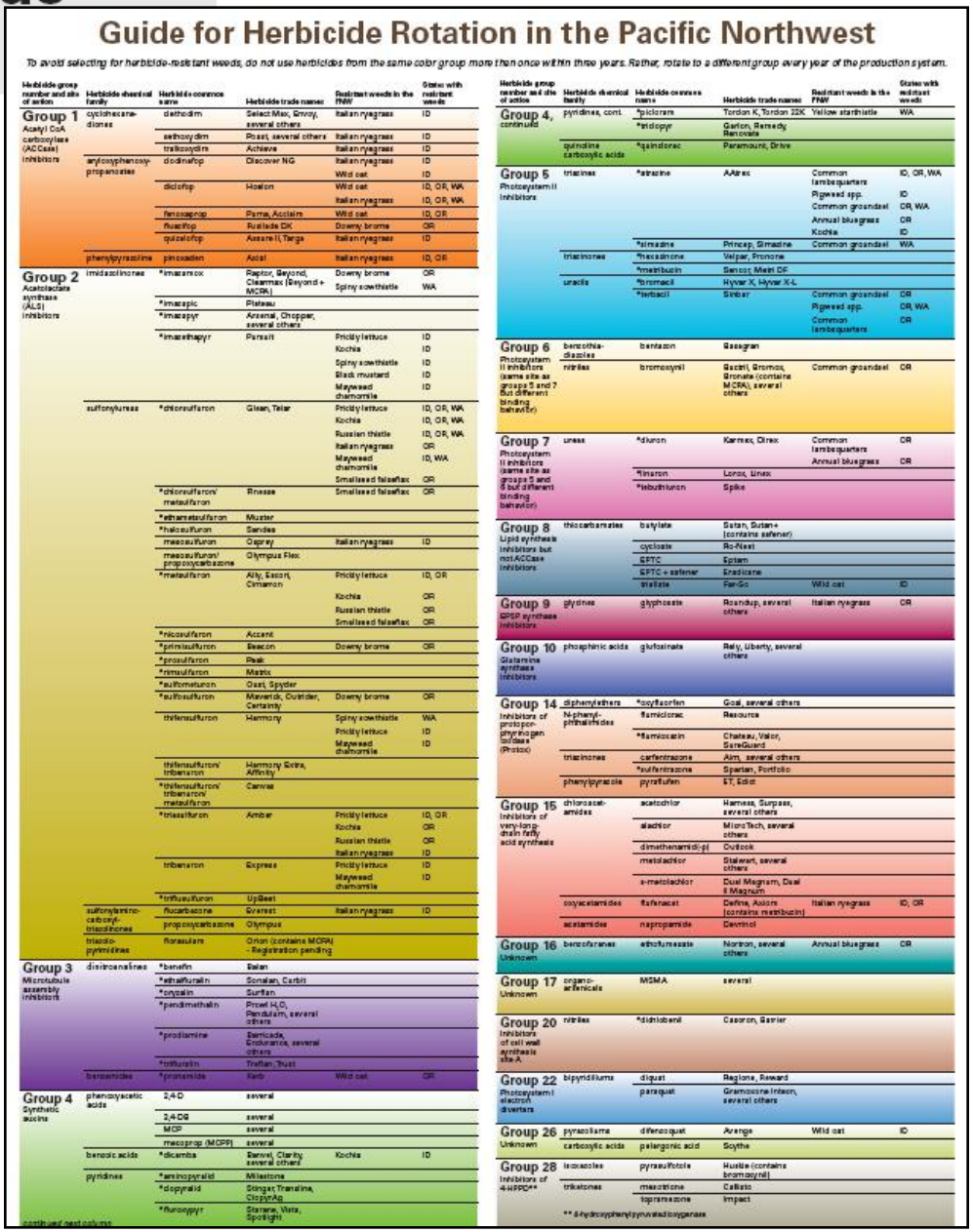

Guide for Herbicide Rotation in the Pacific Northwest

To avoid selecting for herbicide-resistant weeds, do not use herbicides from the same color group more than once within three years. Rather, rotate to a different group every year of the production system.

Herbicide group number and site of action	Herbicide chemical family	Herbicide common name	Herbicide trade names	Resistant weeds in the PNW	States with resistant weeds
Group 1 Acetyl CoA carboxylase (ACCase) inhibitors	cyclohexane-diones	clethodim	Select Max, Envoy, several others	Italian ryegrass	ID
		sethoxydim	Poast, several others	Italian ryegrass	ID
		tralkoxydim	Achieve	Italian ryegrass	ID
	aryloxyphenoxy-propanoates	diclofop	Discover NG	Italian ryegrass	ID
				Wild oat	ID
		diclofop	Hoelon	Wild oat	ID, OR, WA
				Italian ryegrass	ID, OR, WA
		fenoxaprop	Puma, Acclaim	Wild oat	ID, OR
		fluazifop	Fusilade DX	Downy brome	OR
		quizalofop	Assure II, Targa	Italian ryegrass	ID
	phenylpyrazoline	pinoxaden	Axial	Italian ryegrass	ID, OR
Group 2 Acetolactate synthase (ALS) inhibitors	imidazolinones	*imazamox	Raptor, Beyond, Clearmax (Beyond + MCPA)	Downy brome	OR
				Spiny sowthistle	WA
		*imazapic	Plateau		
		*imazapyr	Arsenal, Chopper, several others		
		*imazethapyr	Pursuit	Prickly lettuce	ID
				Kochia	ID
				Spiny sowthistle	ID
				Black mustard	ID
				Mayweed chamomile	ID
	sulfonylurea	*chlorsulfuron	Glean, Telar	Prickly lettuce	ID, OR, WA
				Kochia	ID, OR, WA
				Russian thistle	ID, OR, WA
				Italian ryegrass	OR
				Mayweed chamomile	ID, WA
				Smallseed falseflax	OR
		*chlorsulfuron/ metsulfuron	Finesse	Smallseed falseflax	OR
		*ethametsulfuron	Muster		
		*halosulfuron	Sandea		
		*mesosulfuron	Osprey	Italian ryegrass	ID
		mesosulfuron/ propoxycarbazone	Olympus Flex		
		*metsulfuron	Ally, Escort, Cimarron	Prickly lettuce	ID, OR
				Kochia	OR
				Russian thistle	OR
				Smallseed falseflax	OR
		*nicosulfuron	Accent		
		*primisulfuron	Beacon	Downy brome	OR
		*prosulfuron	Peak		
		*rimsulfuron	Matrix		
		*sulfometuron	Oust, Spyder		
		*sulfosulfuron	Maverick, Outrider, Certainty	Downy brome	OR
		thifensulfuron	Harmony	Spiny sowthistle	WA
				Prickly lettuce	ID
				Mayweed chamomile	ID
		thifensulfuron/ tribenuron	Harmony Extra, Affinity		
		*thifensulfuron/ tribenuron/ metsulfuron	Canvas		
		*triasulfuron	Amber	Prickly lettuce	ID, OR
				Kochia	OR
				Russian thistle	OR
				Italian ryegrass	ID
		tribenuron	Express	Prickly lettuce	ID
				Mayweed chamomile	ID
		*triflusulfuron	UpBeet		
	sulfonylamino-carbonyl-triazolinones	flucarbazone	Everest	Italian ryegrass	ID
		propoxycarbazone	Olympus		
	triazolo-pyrimidines	florasulam	Orion (contains MCPA) - Registration pending		
Group 3 Microtubule assembly inhibitors	dinitroanalines	*benefin	Balan		
		*ethalfluralin	Sonalan, Curbit		
		*oryzalin	Surflan		
		*pendimethalin	Prowl H2O, Pendulum, several others		
		*prodiamine	Barricade, Endurance, several others		
		*trifluralin	Treflan, Trust		
	benzamides	*pronamide	Kerb	Wild oat	OR
Group 4 Synthetic auxins	phenoxyacetic acids	2,4-D	several		
		2,4-DB	several		
		MCP	several		
		mecoprop (MCPP)	several		
	benoic acids	*dicamba	Banvel, Clarity, several others	Kochia	ID
	pyridines	*aminopyralid	Milestone		
		*clopyralid	Stinger, Transline, Clopyralid		
		*fluroxypyr	Starane, Vista, Spotlight		

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Group 4, continued	pyridines, cont.	*picloram	Tordon K, Tordon 22K	Yellow starthistle	WA
		*triclopyr	Garlon, Remedy, Renovate		
	quinoline carboxylic acids	*quinclorac	Paramount, Drive		
Group 5 Photosystem II inhibitors	triazines	*atrazine	AAtrex	Common lambsquarters	ID, OR, WA
				Pigweed spp.	ID
				Common groundsel	OR, WA
				Annual bluegrass	OR
				Kochia	ID
		*simazine	Princep, Simazine	Common groundsel	WA
	triazinones	*hexazinone	Velpar, Pronone		
		*metribuzin	Sencor, Metri DF		
	uracils	*bromacil	Hyvar X, Hyvar X-L		
		*terbacil	Sinbar	Common groundsel	OR
				Pigweed spp.	OR, WA
				Common lambsquarters	OR
Group 6 Photosystem II inhibitors (same site as groups 5 and 7 but different binding behavior)	benzothia-diazoles	bentazon	Basagran		
	nitriles	bromoxynil	Buctril, Bromox, Bronate (contains MCPA), several others	Common groundsel	OR
Group 7 Photosystem II inhibitors (same site as groups 5 and 6 but different binding behavior)	ureas	*diuron	Karmex, Direx	Common lambsquarters	OR
				Annual bluegrass	OR
		*linuron	Lorox, Linex		
		*lobuthiuron	Spike		
Group 8 Lipid synthesis inhibitors but not ACCase inhibitors	thiocarbamates	butylate	Sutan, Sutan+ (contains safener)		
		cycloate	Ro-Neet		
		EPTC	Eptam		
		EPTC + safener	Eradicane		
		triallate	Far-Go	Wild oat	ID
Group 9 EPSP synthase inhibitors	glycines	glyphosate	Roundup, several others	Italian ryegrass	OR
Group 10 Glutamine synthase inhibitors	phosphinic acids	glufosinate	Rely, Liberty, several others		
Group 14 Inhibitors of protoporphyrinogen oxidase (Protox)	diphenylethers	*oxyfluorfen	Goal, several others		
	N-phenyl-phthalimides	flumiclorac	Resource		
		*flumioxazin	Chateau, Valor, SureGuard		
	triazinones	carfentrazone	Aim, several others		
		*sulfentrazone	Spartan, Portfolio		
	phenylpyrazole	pyraflufen	ET, Edge		
Group 15 Inhibitors of very-long-chain fatty acid synthesis	chloroacet-amides	acetochlor	Harness, Surpass, several others		
		alachlor	MicroTech, several others		
		dimethenamid-p	Outlook		
		metolachlor	Stalwart, several others		
		s-metolachlor	Dual Magnum, Dual II Magnum		
	oxyacetamides	flufenacet	Define, Axiom (contains metribuzin)	Italian ryegrass	ID, OR
	acetamides	napropamide	Devrinol		
Group 16 Unknown	benzofuranes	ethofumesate	Nortron, several others	Annual bluegrass	OR
Group 17 Unknown	organo-arsenicals	MSMA	several		
Group 20 Inhibitors of cell wall synthesis site A	nitriles	*dichlobenil	Casoron, Barrier		
Group 22 Photosystem I electron diverters	bipyridiliums	diquat	Reglone, Reward		
		paraquat	Gramoxone Inteon, several others		
Group 26 Unknown	pyrazoliums	difenzoquat	Avenge	Wild oat	ID
	carboxylic acids	pelargonic acid	Scythe		
Group 28 Inhibitors of 4-HPPD**	isoxazoles	pyrasulfotole	Huskie (contains bromoxynil)		
	triketones	mesotrione	Callisto		
		topramezone	Impact		

** 4-hydroxyphenylpyruvatedioxygenase

History

- The discovery of “next gen” herbicides was a very significant accomplishment in the history of weed science

  – historic gains in chemical weed control

- Example:
  – First ALS-inhibitor commercialized in 1982
    - chlorsulfuron (Glean or Telar)
    - broadleaf weed control

Important active ingredients

- Use rates: oz/A vs. lbs/A
- Decline in total active ingredient applied during 80's (Bellinder et al. 1994)

- Broad spectrum
  - soil active
  - wide application windows
  - crop safety
  - low mammalian toxicity

Continued Selection Pressure on Weeds

- Differences in weed control spectrum can be achieved through subtle changes in the chemical structure of herbicides

- Example: ALS inhibitors are continuously being introduced
  - local example: pryroxsulam (PowerFlex) use in wheat
  - > 50 commercial products ?
  - Grass/broadleaf crops, turf, veg management
  - Worldwide

Herbicide Resistance

- Achilles' heel of many of these newer herbicides

- Group 2-ALS Inhibitor example
  - 5 years after commercial introduction in 1987
    - prickly lettuce (Mallory-Smith, 1990)
    - kochia (Primiani, 1990)

Example: ALS Resistant Weeds

- Resistance more common with ALS inhibitors than with any other Group
- ~ 127 species, hundreds of biotypes (Heap, 2012)
- Many local examples across the PNW

Herbicide Resistance

- Herbicide resistance is the result of genetic, biological, ecological and management factors

Herbicide Resistance

- Herbicide resistance is the heritable response of a weed biotype to survive a herbicide treatment to which the wild type population was susceptible

Different Than Herbicide "Tolerance"

- The wild type population was never susceptible to the herbicide
  - glyphosate (Roundup) and common mallow

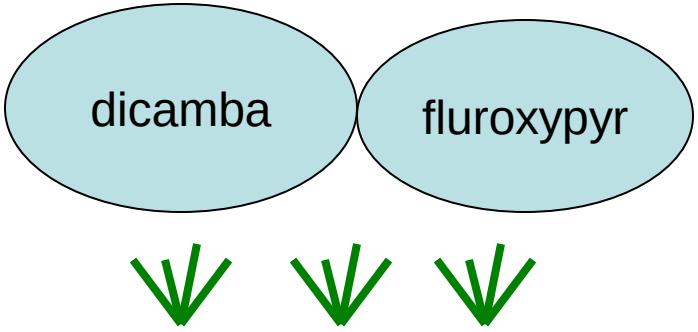
- Selective herbicides are possible because of crop tolerance
  - diclofop (Hoelon) in wheat
  - atrazine in corn

Multiple- and Cross-Resistance

- Cross-resistance is resistance to different herbicides with the same site of action
  - example, imazethapyr (Pursuit) and thifensulfuron (Harmony)
  - Both Group 2 ALS Inhibitors

- Multiple-resistance is resistance to two or more chemically unrelated herbicides with different sites of action
  - example, imazethapyr (Pursuit) and Atrazine
  - Group 2 ALS Inhibitor and Group 5 Photosystem II

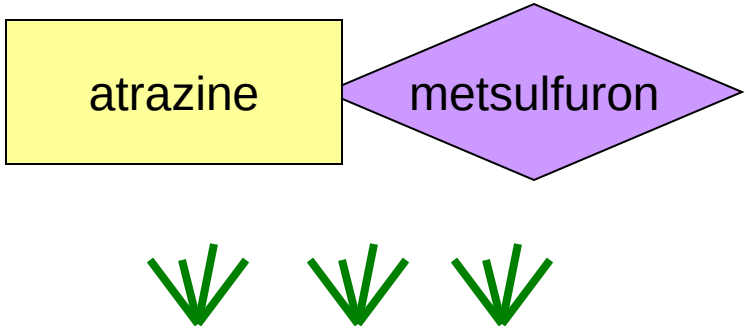
Both herbicides are synthetic auxins



Kochia populations are resistant to dicamba and fluroxypyr

This is an example of cross-resistance.

Atrazine is a triazine and metsulfuron is a sulfonylurea

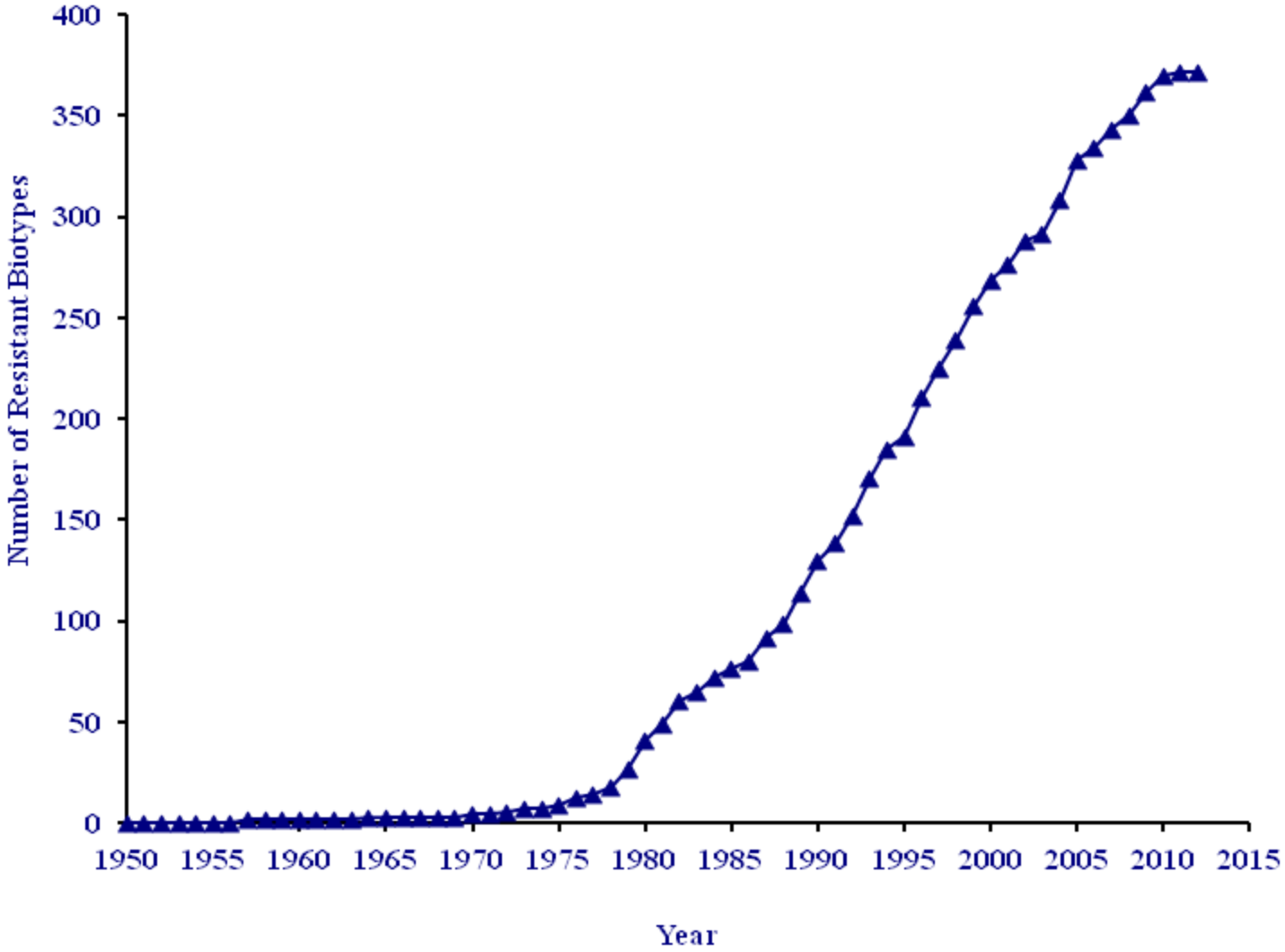


Kochia populations are resistant to atrazine and metsulfuron

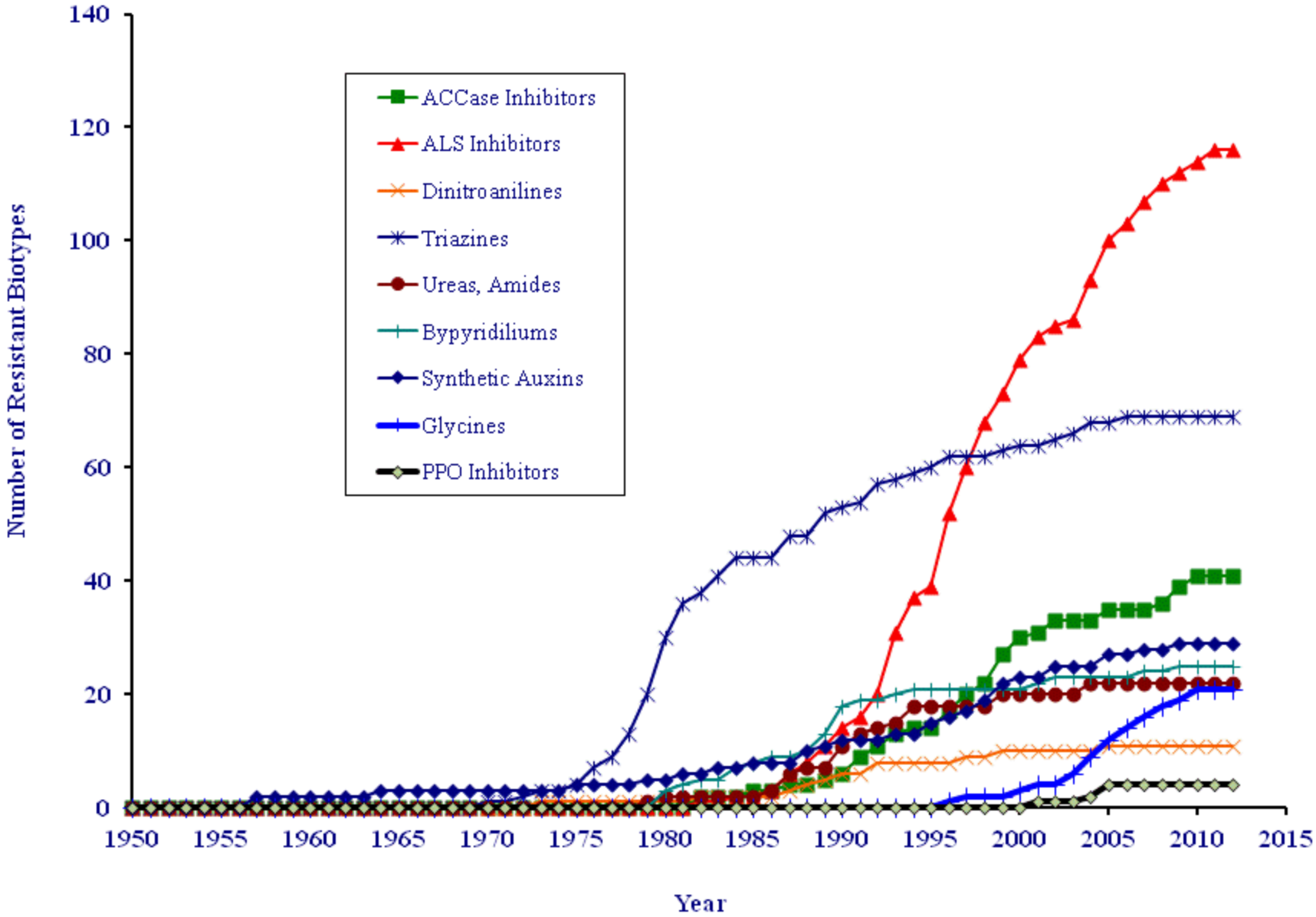
This is an example of multiple-resistance.

Historical Perspective

- 1908 - insecticide resistance
- 1940 - fungicide resistance
- 1957 - herbicide resistance
- 1967 – triazine resistant common groundsel



Source: Ian Heap
http://www.weedscience.com



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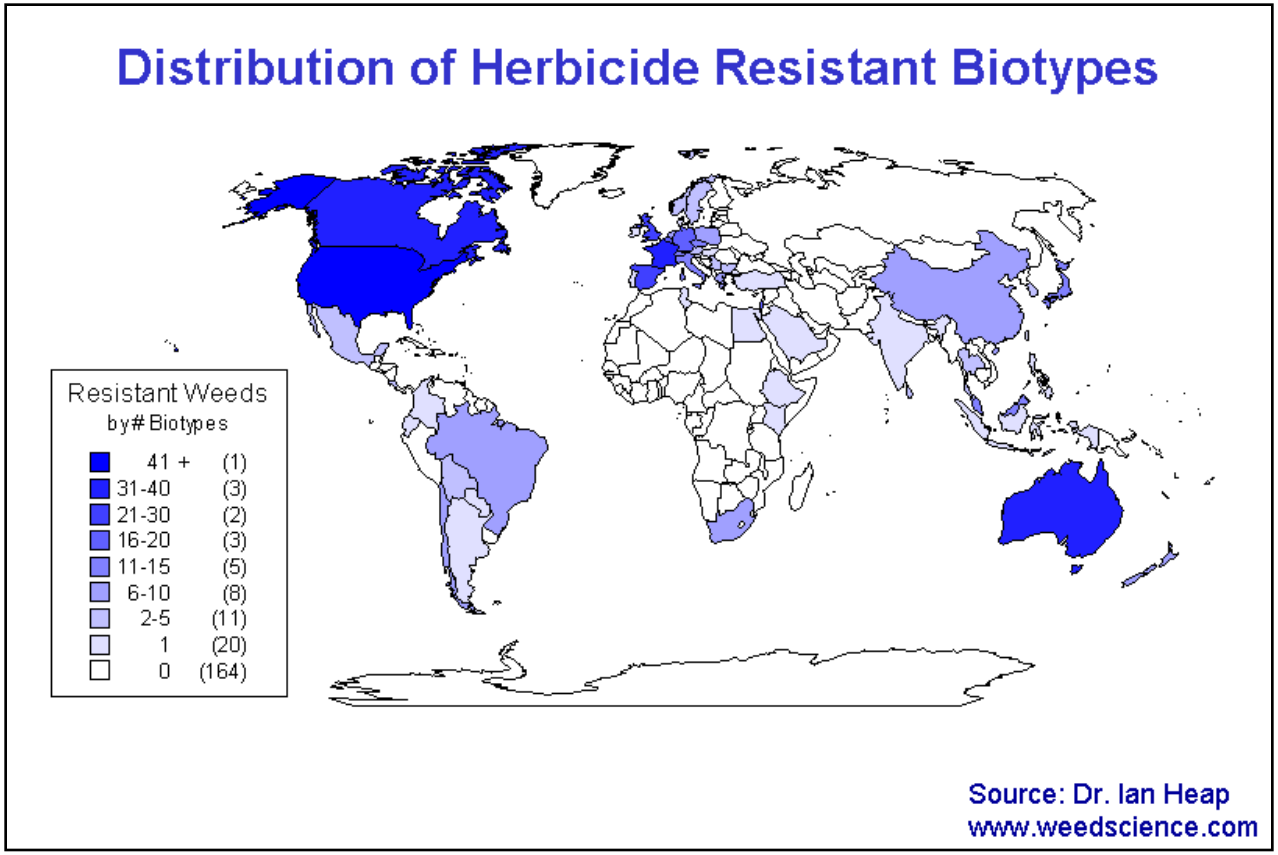
Herbicide Resistant Weeds

- 393 biotypes
- 211 species
  - 124 dicots
  - 87 monocots
- > 680,000 “fields”



Specific Mechanisms of Resistance

- Sequestering – herbicide is kept away from active site
- Decreased uptake / translocation – herbicide does not get into the plant or reach the active site
- Altered target site – herbicide does not bind to the binding/active site
- Detoxification – a change in the ability to metabolize the herbicide

Mechanisms of Resistance

- All mechanisms have been reported but the most common are metabolism and altered target site.

- Glyphosate resistance (Accord/Roundup) is not usually altered target site but is due to changes in translocation or is due to sequestration.

Increased Probability of Resistance

- Single target site
- Extremely effective herbicide
- Long soil persistence
- Frequent or multiple applications

What to Look for in the Field

- No obvious application/environmental problems
- Other weed species are controlled
- Irregular shaped patches
- Records show repeated use of herbicides with the same site of action
- Previous failure at the same site
- No herbicide symptoms on target weed

Herbicide Resistant Weeds in Oregon

- prickly lettuce
- kochia
- Russian thistle
- wild oat
- Italian ryegrass
- common lambsquarters
- annual bluegrass
- pigweed spp.
- common groundsel
- downy brome
- small-seeded falseflax

Likely Many Others?

Resistance Summary

- Oregon situation is somewhat unique in that the crop and the weed are sometimes the same species
- Multiple-resistance is becoming more common than resistance to a single herbicide or cross-resistance
- At this point, predicting multiple-resistance is not possible
- Herbicide rotation as the sole management strategy is no longer a valid recommendation because resistance patterns are unknown

Challenges We Are Addressing

- How do we make site specific recommendations?
  - Not practical to test every population with all possible herbicides
- Are resistance mechanisms independent of each other?
- How many genes are involved and are traits dominant?
- Are cases of multiple-resistance due to gene flow between populations?

What To Do If You Suspect Resistance

- Review WSSA BMP's for resistance management: http://wssa.net/weed/resistance/

- Do not re-spray with a herbicide with the same site of action

- Do not use a higher rate of the same herbicide

- Document resistance
  - Confirm the type of resistance present if possible

Prevention & Management

- Limit applications of herbicides with the same site of action

- Use tank-mixtures or sequential treatments of herbicides

Prevention and Management

- Prevention is the best strategy
- Requires
  - knowledge of the herbicide
    - need to know the herbicide site of action
    - need to know about persistence
    - need to know the control spectrum
  - knowledge of the weed biology
  - willingness to change system

Prevention & Management

- Prevent resistant weeds from producing seeds

- Clean equipment before leaving an area with resistant weeds

Herbicide Resistance in the 21st Century

- More weed species will develop resistance
- Resistance to most if not all herbicides will occur

Herbicide Resistance in the 21st Century

- Herbicides will still be used as the primary weed control method for the foreseeable future

- No herbicides have been removed from the marketplace because of resistance

- However, growers have lost the use/value of herbicides for control of specific weeds at some sites

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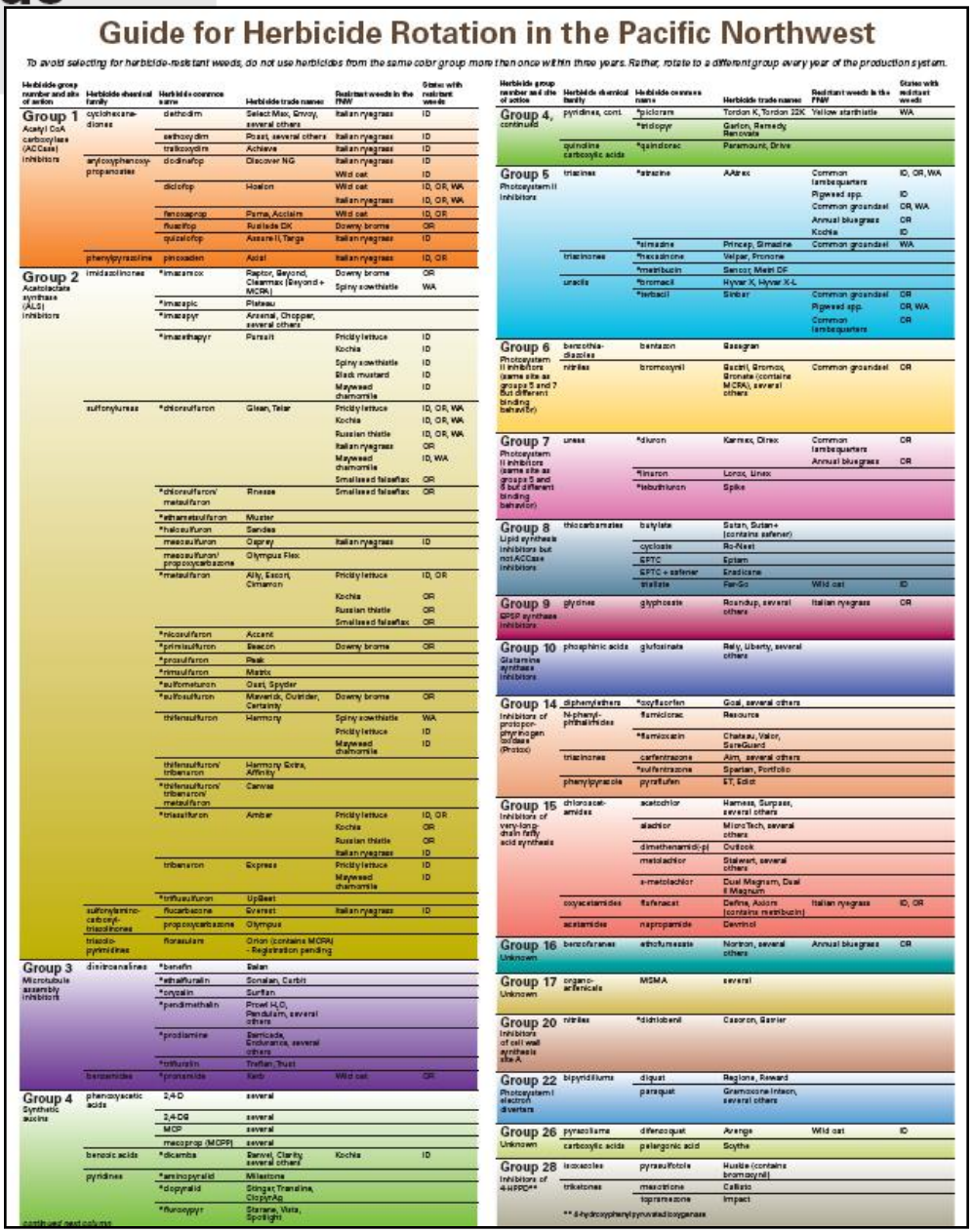

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		triallate	Far-Go	Wild oat	ID
Group 9 EPSP synthase inhibitors	glycines	glyphosate	Roundup, several others	Italian ryegrass	OR
Group 10 Glutamine synthase inhibitors	phosphinic acids	glufosinate	Rely, Liberty, several others		
Group 14 Inhibitors of protoporphyrinogen oxidase (Protox)	diphenylethers	*oxyfluorfen	Goal, several others		
	N-phenyl-phthalimides	flumiclorac	Resource		
		*flumioxazin	Chateau, Valor, SureGuard		
	triazinones	carfentrazone	Aim, several others		
		*sulfentrazone	Spartan, Portfolio		
	phenylpyrazole	pyraflufen	ET, Edge		
Group 15 Inhibitors of very-long-chain fatty acid synthesis	chloroacet-amides	acetochlor	Harness, Surpass, several others		
		alachlor	MicroTech, several others		
		dimethenamid-p	Outlook		
		metolachlor	Stalwart, several others		
		s-metolachlor	Dual Magnum, Dual II Magnum		
	oxyacetamides	flufenacet	Define, Axiom (contains metribuzin)	Italian ryegrass	ID, OR
	acetamides	napropamide	Devrinol		
Group 16 Unknown	benzofuranes	ethofumesate	Nortron, several others	Annual bluegrass	OR
Group 17 Unknown	organo-arsenicals	MSMA	several		
Group 20 Inhibitors of cell wall synthesis site A	nitriles	*dichlobenil	Casoron, Barrier		
Group 22 Photosystem I electron diverters	bipyridiliums	diquat	Reglone, Reward		
		paraquat	Gramoxone Inteon, several others		
Group 26 Unknown	pyrazoliums	difenzoquat	Avenge	Wild oat	ID
	carboxylic acids	pelargonic acid	Scythe		
Group 28 Inhibitors of 4-HPPD**	isoxazoles	pyrasulfotole	Huskie (contains bromoxynil)		
	triketones	mesotrione	Callisto		
		topramezone	Impact		

** 4-hydroxyphenylpyruvatedioxygenase

Synthetic Auxins-Group 4

Mode of Action

– These herbicides disrupt hormone balance and protein synthesis in plants, leading to a variety of plant growth abnormalities

Chemical Families

– Phenoxy Acetic Acids: 2,4-D, 2,4-DB, MCP

– Benzoic Acids: dicamba (Banvel)

– Pyridines: fluroxypyr (Starane), picloram (Tordon), clopyralid (Stinger), triclopyr (Garlon 4), aminopyralid (Milestone)

Synthetic Auxins-Group 4

Site of Action

– Site(s) of action is unknown, believed to have multiple sites of action

Translocation

– Extensively translocated in xylem and phloem, herbicides accumulate in newest leaves and meristems

Drift, volatilization, and tank contamination are common, especially with ester formulations of these products.

Synthetic Auxins-Group 4

Uses / Notes

– Primarily “broadleaf killers,” used for postemergence broadleaf control in corn, wheat, rye, barley, turf, pasture, roadsides

– Often have some soil activity

Symptoms

Broadleaf weeds / crops:

– Stem twisting and epinasty (downward twisting)

– Leaf malformations (leaf cupping, crinkling, strapping (parallel veins), puckering, bubbling)

– Callus tissue formation

Leaf rolling

Stem twisting

Fused brace roots in corn

Amino Acid Synthesis Inhibitors-Group 2

Mode of Action

– Inhibits a specific enzyme (single site) which prevents production of essential amino acids

Chemical Families

– Imidazolinones: imazethapyr (Pursuit), imazamox (Beyond)

– Sulfonylureas: sulfometuron (Oust), chlorimuron (Classic), nicosulfuron (Accent), primisulfuron (Beacon), thifensulfuron (Harmony GT), halosulfuron (Permit), chlorsulfuron (Glean), mesosulfuron (Osprey)

Amino Acid Synthesis Inhibitors-Group 2

Chemical Families, con't.

- Sulfonanilides: cloransulam-methyl (FirstRate)

- Sulfonylaminocarbonyl-triazolinone:
  flucarbazone (Everest)
  propoxycarbazone (Olympus)

Amino Acid Synthesis Inhibitors-Group 2

Site of Action

– Imidazolinones, Sulfonylureas, and Sulfonanilides prevent production of three essential amino acids by inhibiting the same enzyme, acetolactate synthase (ALS)

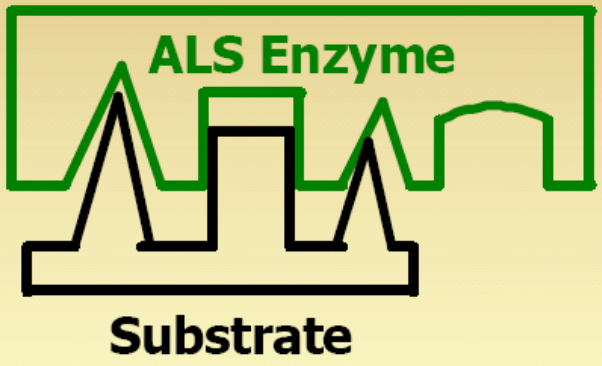
Translocation

– Move through xylem and phloem and accumulate in meristematic region, will see injury on new leaves

ALS Inhibition

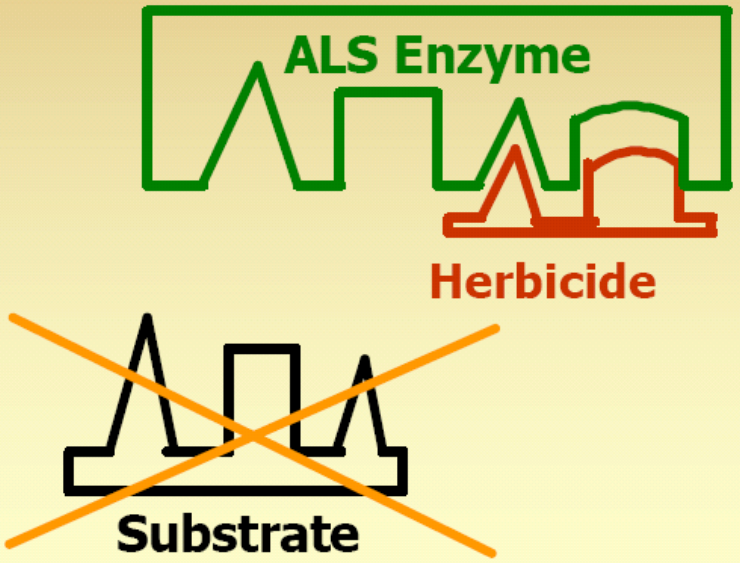
ALS Enzyme Action

- substrate binds to enzyme



Inhibition of ALS Enzyme

- herbicide blocks normal substrate



Amino Acid Synthesis Inhibitors-Group 2

Uses / Notes
– PRE/POST weed control in various crops
– Immediate growth cessation
– Slow to develop, gradual chlorosis followed by necrosis of newest growth after several days
– Death of growing point
– Stunting, slow growth, death of plant may take up to 28 days
– IMI’s and SU’s are difficult to distinguish

Amino Acid Synthesis Inhibitors-Group 2

Symptoms, con't.

Broadleaf symptoms:

– Stunting, chlorosis, and purpling of the leaves
– Red or purple veins on the underside of broadleaf leaves (unique to IMI's and SU's)
– Irregular leaf shape (crinkled, puckered, and/or drawstring effect)
– Proliferation of additional shoots, new leaves are small
– Shortened internodes

Red or purple leaf veins

EPSP Synthase Inhibitors-Group 9

Mode of Action

– Inhibits a specific enzyme (single site) which prevents production of essential amino acids

Chemical Familiy

– Glycines : glyphosate

(RoundUp formulations and others)

EPSP Synthase Inhibitors-Group 9

Site of action

– Glycines prevent production of three other essential amino acids by inhibiting EPSP Synthase

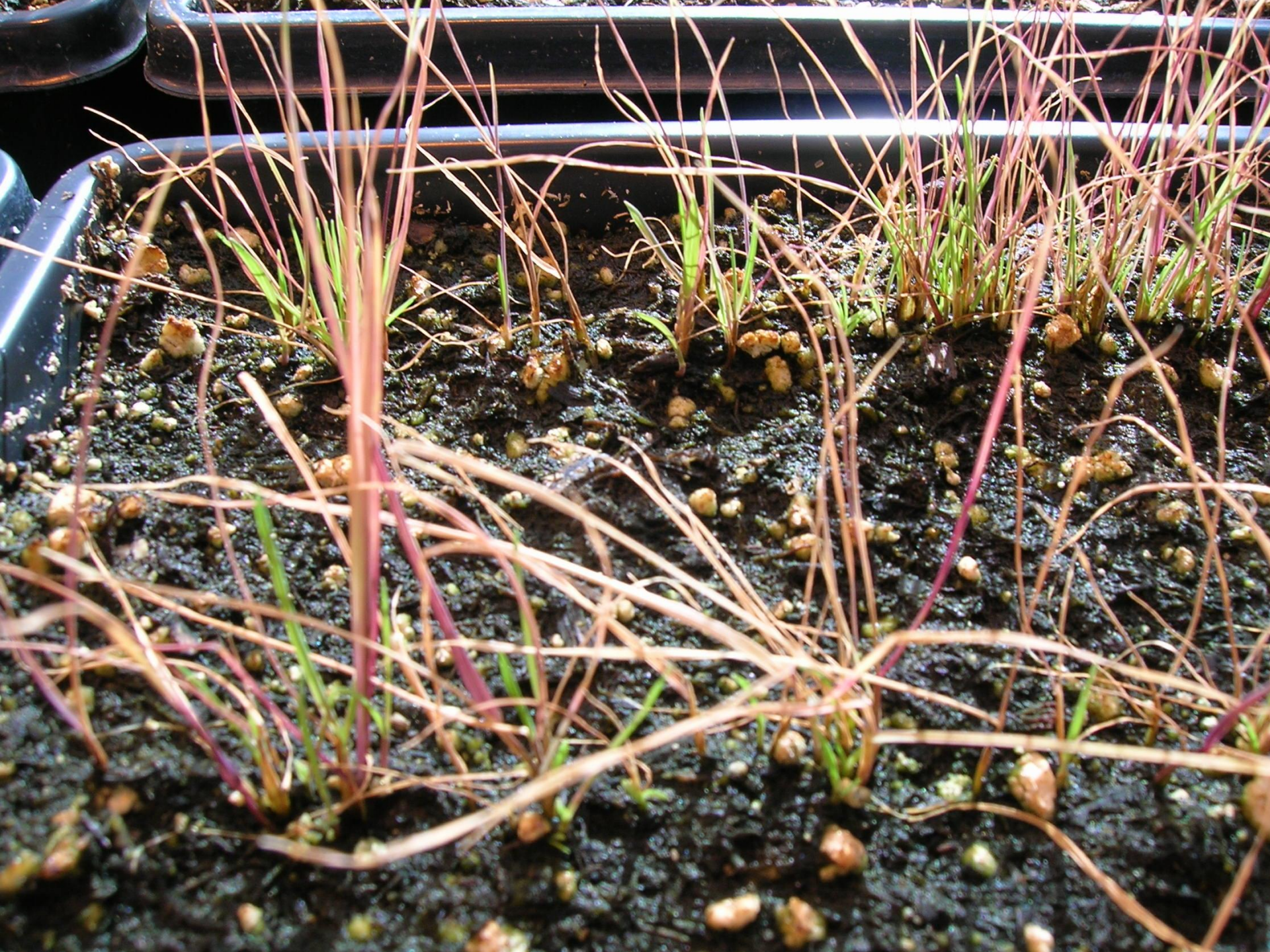
Translocation

– Move through xylem and phloem and accumulate in meristematic region, will see injury on new leaves

EPSP Synthase Inhibitors-Group 9

Uses / Notes

– Burndown applications preplant or chem fallow
– POST weed control in various glyphosate-tolerant crops
– Nonselective spot spraying applications
– Slow to develop, gradual chlorosis followed by necrosis of newest growth after several days
– Death of growing point
– Stunting, slow growth, death of plant may take up to 28 days



ACCase Inhibitors-Group 1

Mode of Action
– Prevents the formation of fatty acids, which are essential for the production of lipids. Lipids are vital in the integrity of cell membranes and thus new plant growth

Chemical Families
– Cyclohexanediones: clethodim (Select)
– Aryloxyphenoxypropionates: quizalifop (Assure)
– Phenylpyrazoline: pinoxaden (Axial)

ACCase Inhibitors-Group 1

Site of Action
– Inhibits the ACCase enzyme which ceases the synthesis of fatty acids

Translocation
– Symplastic movement - translocate to all areas of new growth via phloem, no soil activity

Uses / Notes
– Postemergence “grass killers” , no BL activity
– Control many annual and perennial grasses

ACCase Inhibitors-Group 1

Symptoms

Only on Grasses:

– Injury first appears on new emerging whorl leaves

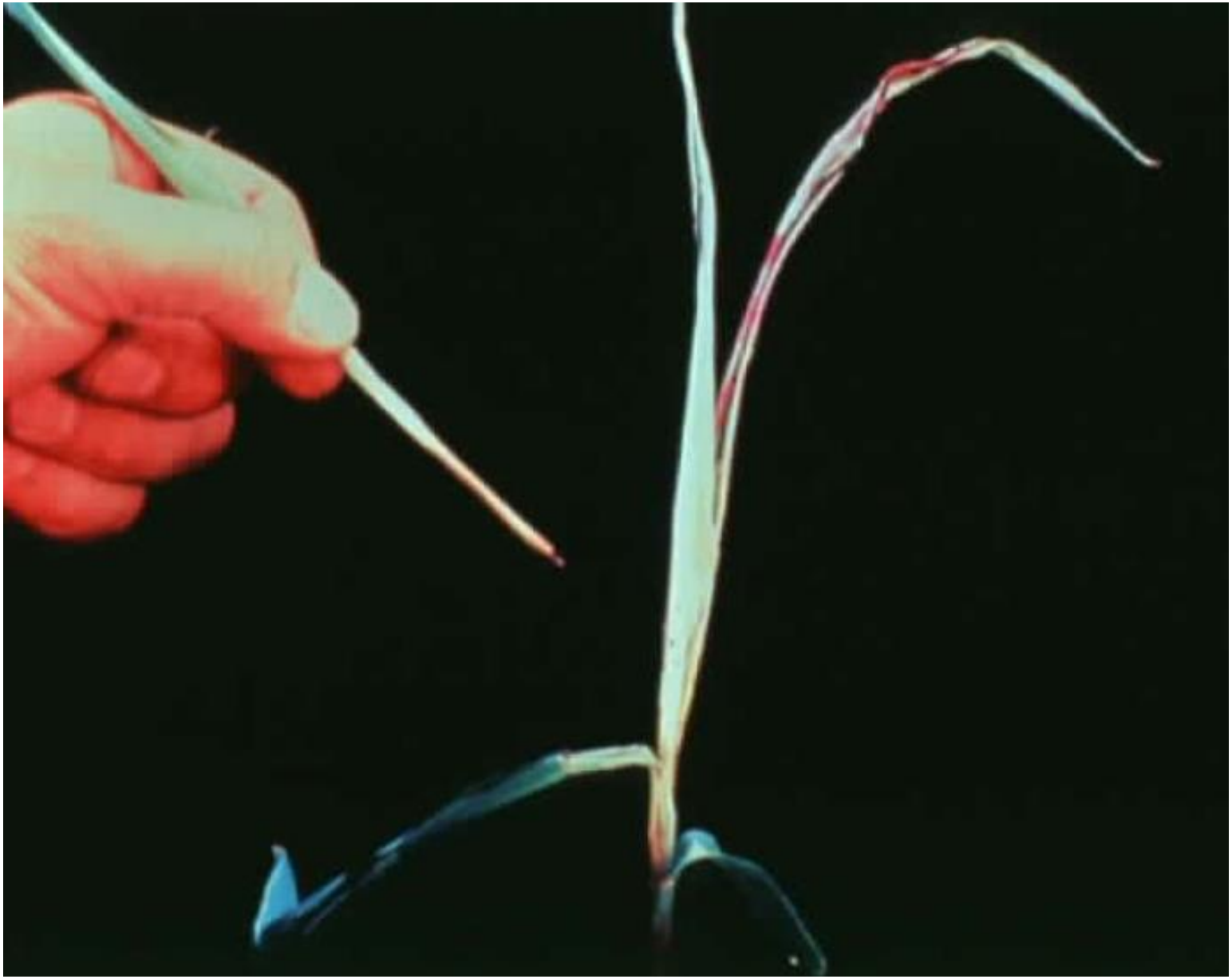
– Immediate growth stoppage

– Very gradual discoloration of tissue

– Slow acting, symptoms take 7 to 14 days to show up

– Chlorosis to reddening followed by necrosis of grass whorl

– Can pull out dead whorl, an early indicator (growing point separates from rest of the plant)



Necrosis of growing point

PPO Inhibitors-Group 14

Mode of Action
– These herbicides disrupt cell membranes

Chemical Families
– Bipyridyliums: paraquat (Gramoxone)
– Diphenylethers: oxyfluorfen (Goal)
– N-phenylphthalimides: Flumioxazin (Chateau)
– Aryltriazolinones: carfentrazone-ethyl (Aim)
  sulfentrazone (Spartan)

PPO Inhibitors-Group 14

Site of Action
– Light causes the formation of free radicals. These radicals rupture plant cell membranes resulting in a rapid browning of tissue

Translocation
– None or very limited, necrotic spots

Uses / Notes
– Mostly foliar-applied - uptake into leaves
– Some soil-applied - root and shoot uptake

PPO Inhibitors-Group 14

Symptoms

– Symptoms vary somewhat with herbicide and spray additive

– Rapid necrosis of plant tissue (1 to 2 hours)

– Leaves may have a water-soaked appearance or burned appearance followed by wilting an rapid desiccation

– Burnt, crispy brown tissue, leaf speckling

– Only kills the tissue it comes into contact with

– Plant parts not covered my survive

– Activity increases with sunlight, temperature, and humidity

Water soaked spots

Necrosis of leaf tissue

Necrosis of leaf tissue