How Herbicides Work and Where They Go

Fred Fishel

Professor, UF/IFAS Agronomy

Herbicides 101

- Herb-i-cide: “plant” and “kill”
- 2,4-D discovered in the 1940s: modern era of chemical weed control
- 2,4-D use occurred from a few thousand acres in 1946 to several million acres 4 years later
- Most of the chemicals used prior to 2,4-D were inorganic
- All of those introduced since 2,4-D are organic

Early History of Herbicides

- Germany:
  - 1840: lime recommended for control of horsetail
  - 1854: salt recommended as a herbicide
- 1937-1950: salt used extensively for field bindweed control along Kansas R-O-Ws

The usual rate of salt was 20 tons/A!!!

Early History of Herbicides

- 1896: copper sulfate used for selective weed control of charlock in wheat by the French
- 1890's: copper sulfate, iron sulfate, sulfuric acid, and nitric acid were tested in the US
- Copper sulfate: most widely used algaecide in US since 1905
- 1935: sulfuric acid used in U.S. for weed control in onions and cereals

Tended to desiccate plants by water removal

Poison Ivy Control

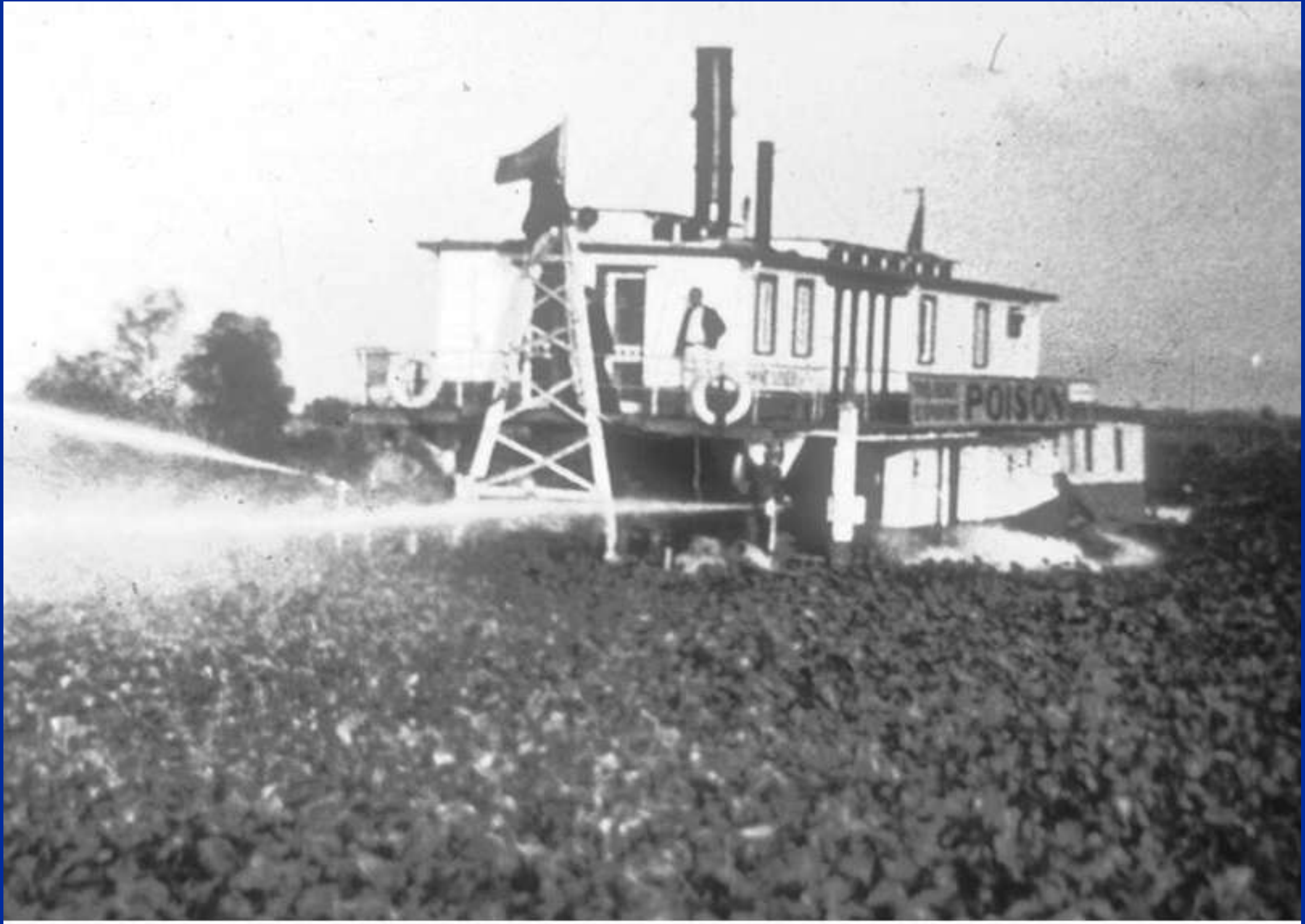
New Jersey Agricultural Experiment Station Circular 206 (1927)

- “Sulfuric, hydrochloric and nitric acids are positively destructive to the plant.”
- “…care must be exercised in their use, for they will burn clothing and flesh instantly. They will also result in blindness if spattered into the eyes.”

Early History of Herbicides

- 1902-1945: arsenicals used for weed control
  - Nonspecific inhibitors of enzymes containing sulfhydryl groups and uncouplers of oxidative phosphorylation
  - Louisiana – Florida: Aquatic weeds (water-hyacinth and submersed aquatic weeds – sodium arsenite)
    - Toxic to humans, livestock, and wildlife
  - Hawaii: Annual weeds (1913 – 1945)
  - California: Perennial weeds (field bindweed)
    - Demonstrated early evidence of translocation

Early History of Herbicides



Poison Boat on the St Johns River

Poison Ivy Control

New Jersey Agricultural Experiment Station Circular 206 (1927)

- "Arsenate of soda is a dangerous poison…"
- "Under no circumstances should he (applicator) permit any of the material to get into his mouth or nose. This danger can be overcome by wearing a small wet sponge or fine piece of cloth over the nose while working the sprayer."

Early History of Herbicides

- Other herbicides of the “pre- 2,4-D” era:
  - Sodium chlorate (1925 – 1930)
    - Soil sterilant at high rates, cotton defoliant at low rates
    - Flammable
    - Still used today – defoliant/desiccant formulated with a flame retardant
  - Sulfuric acid
    - Use limited due to corrosiveness to metal spray rigs

The Control of Weeds

California Agricultural Extension Service Circular 54 (1931)

- Chlorates are fire hazard (oxidizer)
  - “Clothing, chaff, straw, sacks, wood, etc., covered with chlorate will readily ignite when dry.”
  - “Ashes from smoking tobacco, a match thoughtlessly lighted, or a spark from an exhaust pipe of spray equipment may set a fire.”
  - “Men should not work alone when using chlorates.”

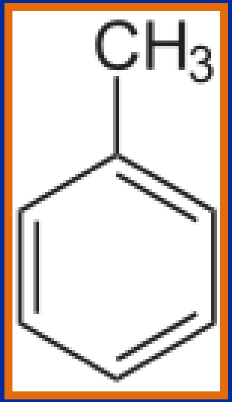
Early History of Herbicides

- Queen Victoria

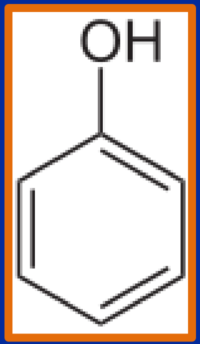
Jack the Ripper

Early History of Herbicides

- Coal tar
- Phenols
- Toluene
- Pyridine

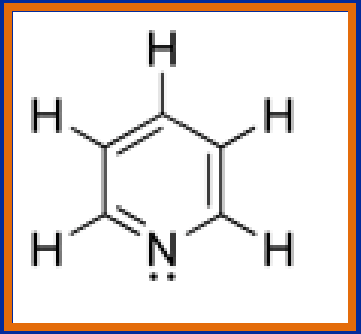


Toluene



Phenol

Pyridine



Early History of Herbicides

The discovery of the phenoxyacetics during 1942 to 1944 marked the real beginning of the herbicide phase of the "Chemical Era of Agriculture."

Early History of Herbicides

The use of organic herbicides for weed control is in its infancy if compared to other advances in agricultural technology, such as soil fertility and plant breeding.

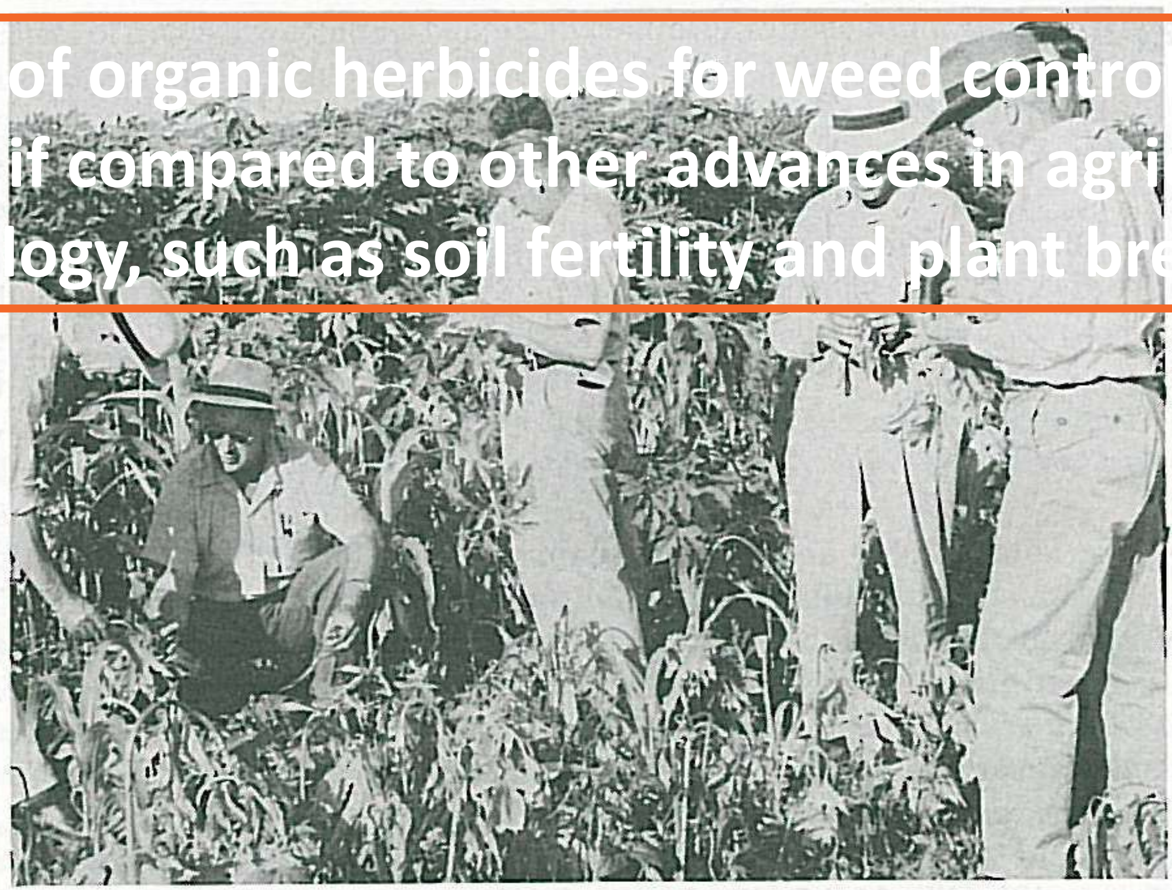


Figure 16-1. Scientists studying the selective killing of giant ragweed in corn in Henderson County, Kentucky, 1947. This was one of the first large-scale tests made with 2,4-D in the United States. (Sherwin-Williams Company.)

Early History of Herbicides

- Reasons modern herbicide use expanded rapidly:
  - Low use rates (not tons)
  - low volumes of water – equally effective as high volumes
  - Biological selectivity – broadleaves in grassy crops
  - Private industry’s role
    - Development of effective formulations
    - Development of manufacturing processes
    - Marketing through effective distribution networks

Herbicides 101

- All
- Do
- Pla ent fro
- He pla ve these systems, we are generally not affected

Herbicide Active Ingredient	Rat Oral LD_{50}
Paraquat	150
2,4-D (sodium salt)	700
Atrazine	1869
Glyphosate	>5000
Imazapyr	>5000

Herbicides 101

- How do plants grow?
  - Photosynthesis
  - Respiration

Table 1.
Comparison of photosynthesis and respiration

Photosynthesis	Respiration
Produces sugars from light energy	Burns sugars for energy
Stores energy	Releases energy
Occurs only in cells with chloroplasts	Occurs in most cells
Releases oxygen	Uses oxygen
Uses water	Produces water
Uses carbon dioxide	Produces carbon dioxide
Requires light	Occurs in dark and light

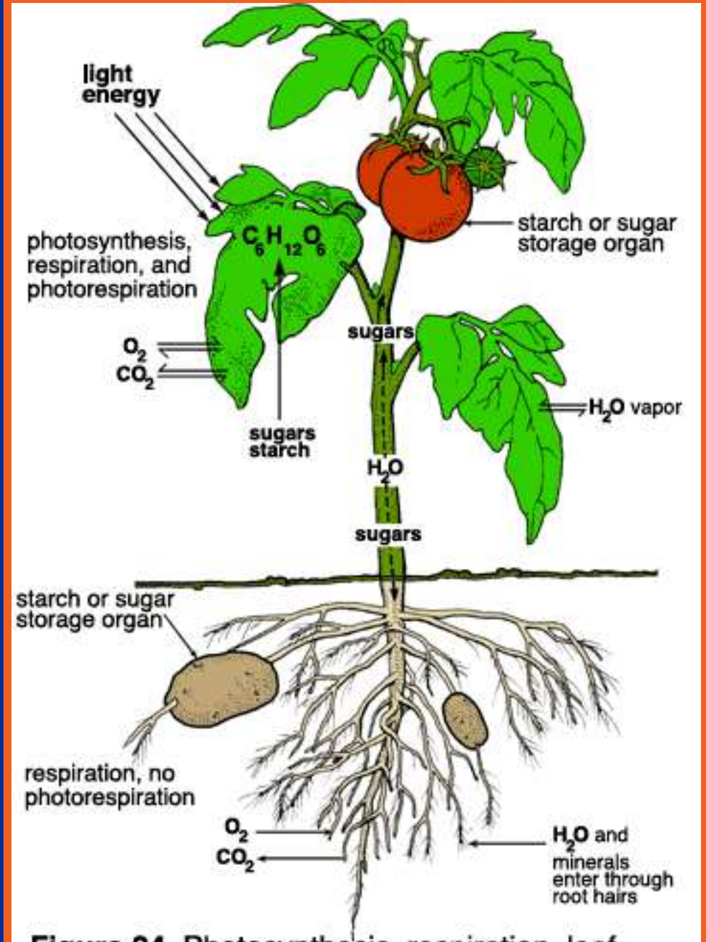


Figure 24. Photosynthesis, respiration, leaf water exchange, and translocation of sugar (photosynthate) in a plant.

Herbicides 101

- When a herbicide contacts a plant…..
  - Processes
    - Absorption
    - Translocation
    - Molecular fate of the herbicide in the plant
    - Effect of the herbicide on metabolism

When one plant species is more tolerant to the chemical than another plant species, then the chemical is considered to be selective

Herbicide Classification

- **How are herbicides classified?**
  - ***Mode of Action***
  - **Time of application**
  - **Uptake characteristics**
  - **Selectivity**
  - **Persistence**

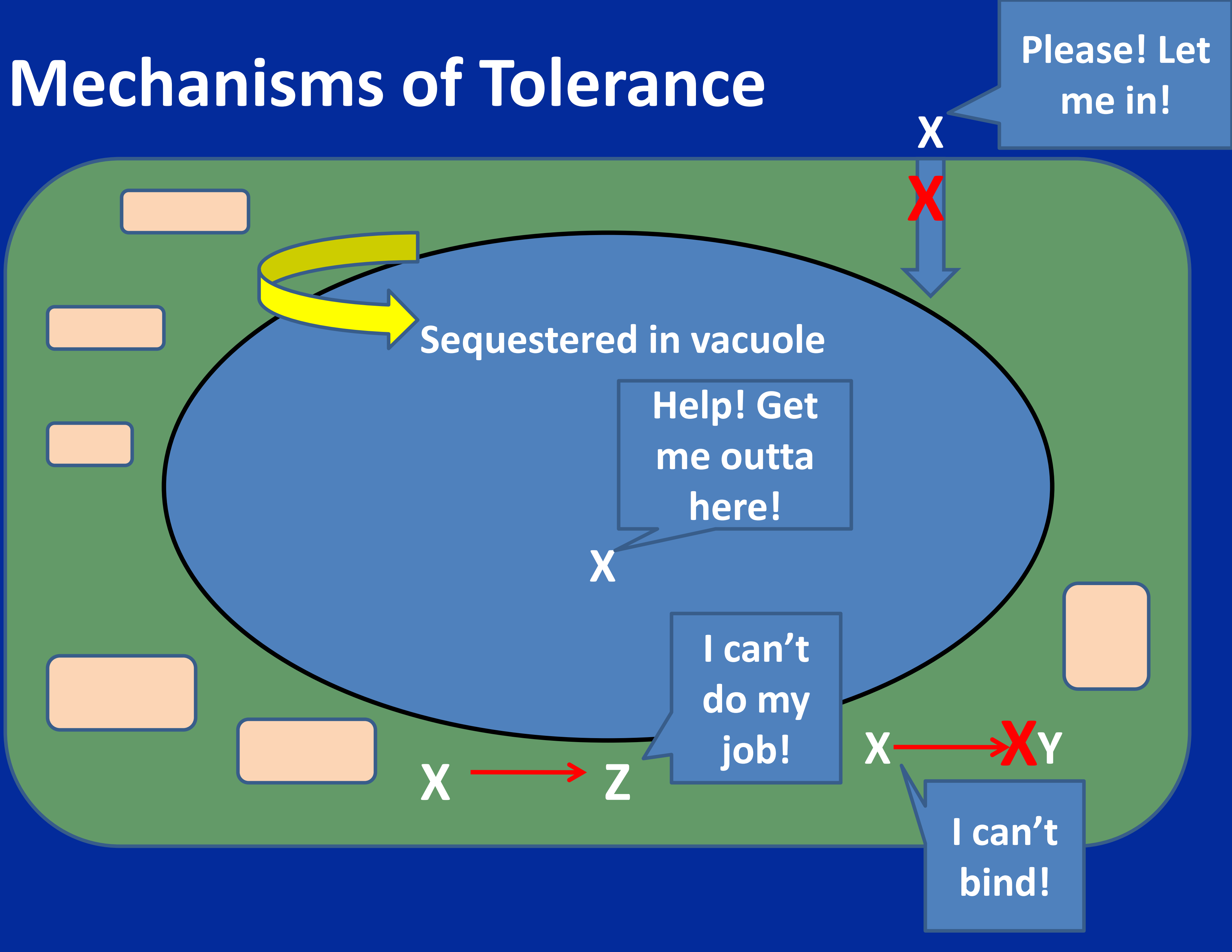
Terminology

- **Mode of action:** the way by which a herbicide may alter or adversely affect physiological or biochemical events in a weed resulting in a toxic effect, usually ending in death
- **Mechanism of action:** the specific process inhibited by a herbicide; the actual biochemical site of activity

Terminology

- <u>Resistant:</u> originally susceptible to herbicide; over time control lost through the selection of resistant plants
- <u>Tolerant:</u> species never susceptible to herbicide at label use rates

Mechanisms of Tolerance



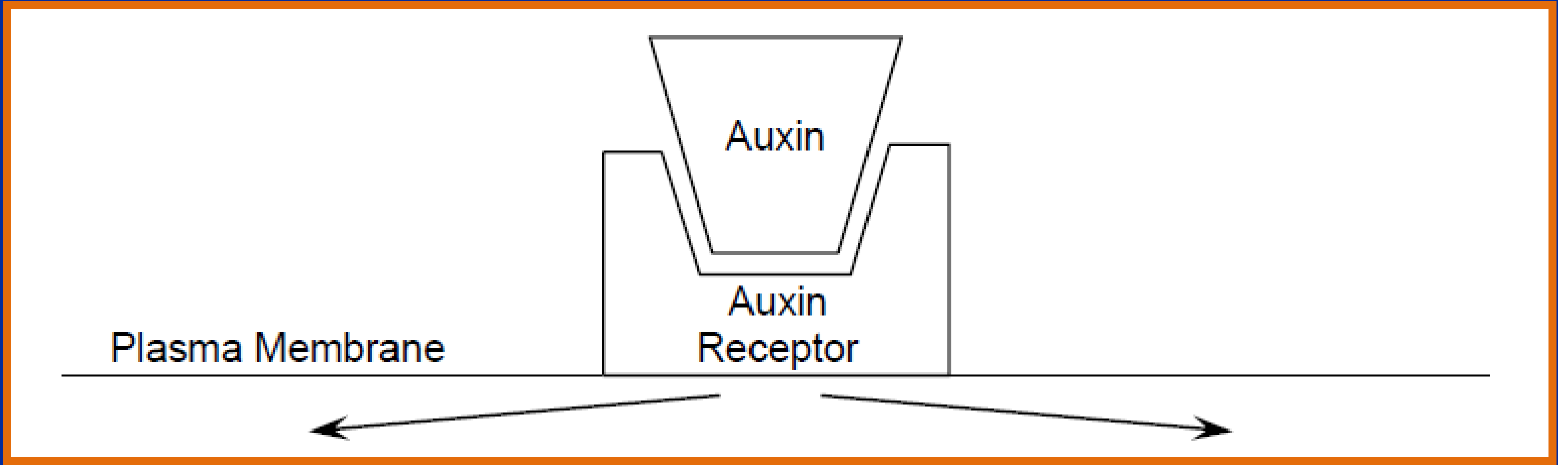
Herbicide Mode of Action Groups

- Photosynthesis inhibition
- Amino acids and proteins inhibition
- Fatty acid synthesis inhibition
- Growth inhibition
- Cell membrane formation inhibition
- Pigment synthesis inhibition
- Growth regulation

Growth Regulation

- **Phenoxy-Carboxylic Acids:**
  - 2,4-D
  - 2,4-DB
- **Benzoic Acids:**
  - Dicamba
- **Pyridine Carboxylic Acids:**
  - Aminopyralid
  - Aminocyclopyrachlor
  - Triclopyr
- **Quinoline Carboxylic Acids:**
  - Quinclorac

Synthetic Auxin Herbicides



- Increased RNA polymerase activity
- Increased RNA and protein synthesis
- Cell wall loosening and cell enlargement
- Uncontrolled cell division and growth
- Increased ethylene production
- Vascular tissue plugging

Synthetic Auxin Herbicides

2,4-D

- Postemergence in grassy crops including:
  - Corn, turf, sugarcane
  - Selectivity based upon metabolism
    - Susceptible plants activate them into the acid form
    - Tolerant plants do not metabolism into an active form
  - Readily plant absorbed
  - Readily translocated in the living tissues (phloem)
  - Short persistence with an average half-life of 10 days

Resistance Concerns in Southeast U.S.

- None presently with 2,4-D…..but
  - Barnyardgrass resistance to quinclorac in Arkansas rice
- 1st recorded herbicide-resistant weed was 2,4-D resistant spreading dayflower in sugarcane in Hawaii in 1957
- Resistance chances are slim because these herbicides probably act on multiple plant processes

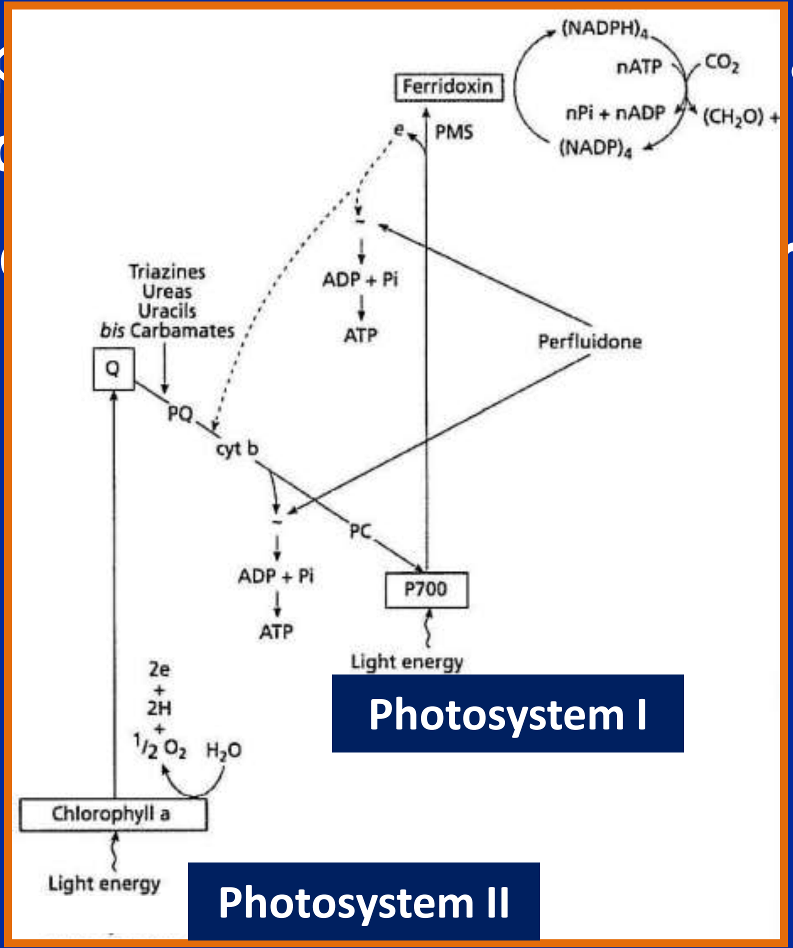
Photosynthesis

$$CO_2 + 2H_2O \xrightarrow[\text{Chlorophyll}]{} CH_2O + H_2O + O_2$$

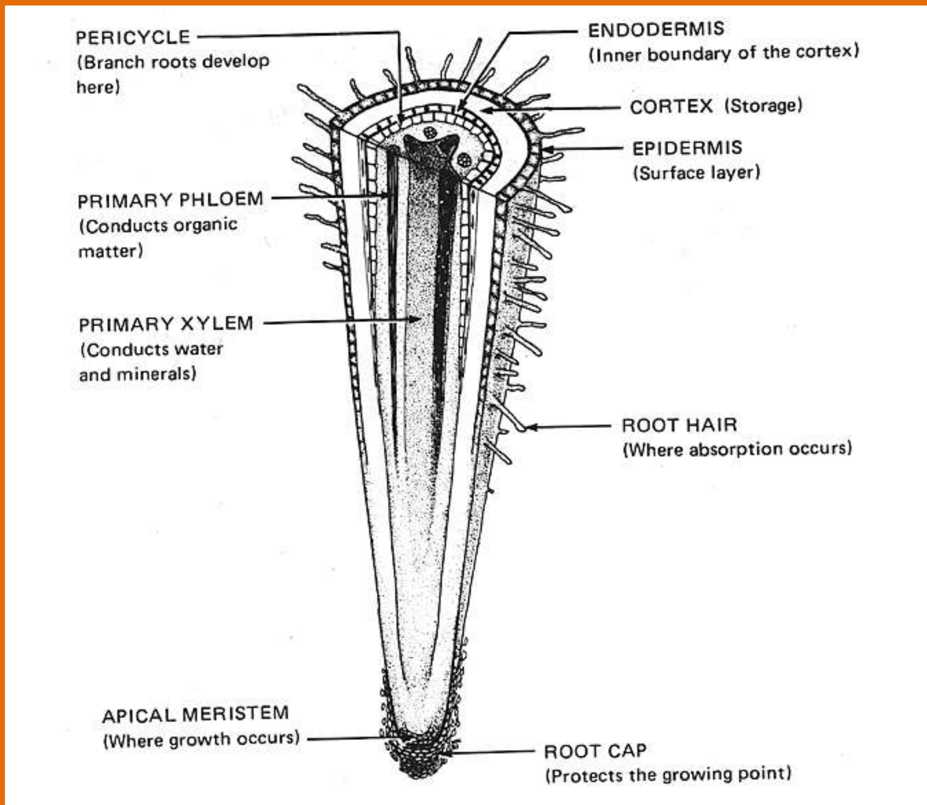
Inhibition of Photosynthesis

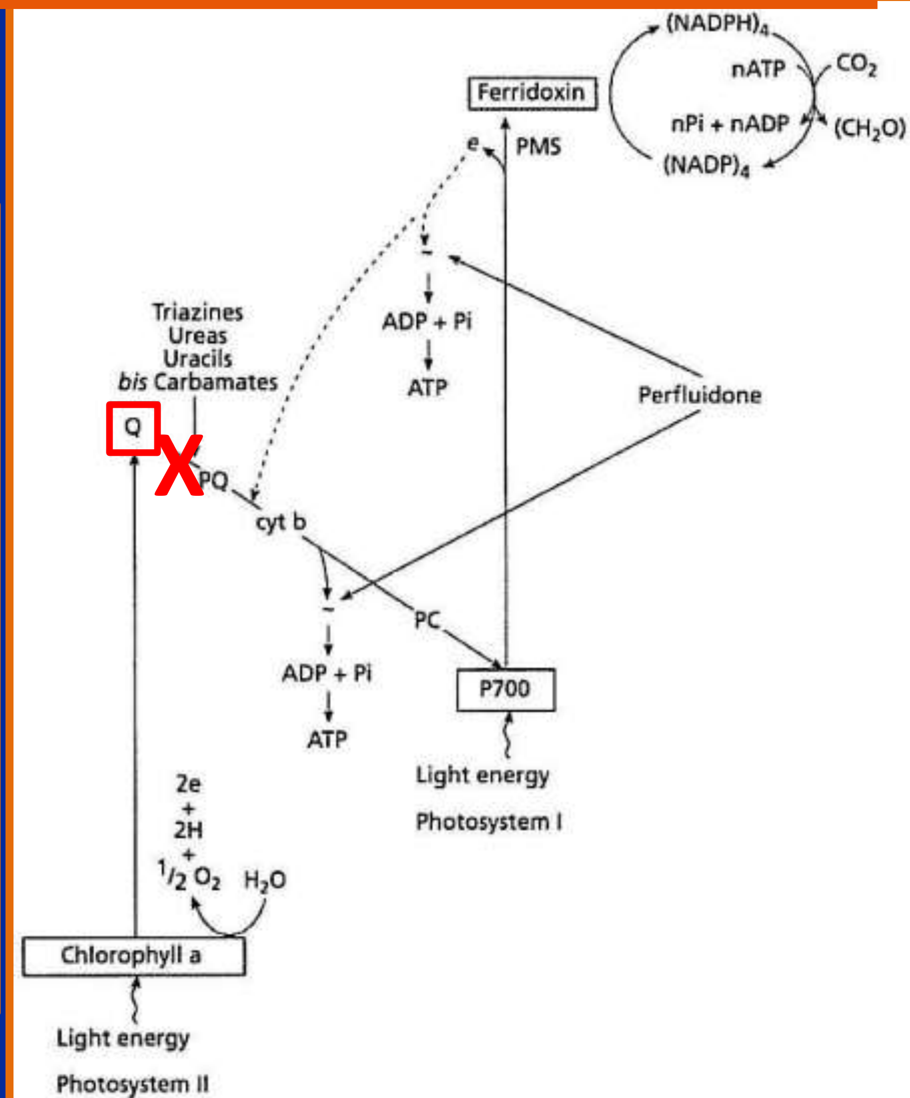
- Photosynthesis-inhibiting herbicides…..
  - Misconception: suscep ath” because they can no lo
  - Fact: plants die long be re depleted

Photosynthetic transport chain
“Z scheme”



Inhibition of Photosynthesis at Photosystem II





Inhibition of Photosynthesis at Photosystem II: Triazines

- Examples of FL importance:
  - Atrazine
    - Most widely used herbicide in the U.S. in pounds applied
    - Preemergence control of broadleaf weeds
    - FL – important use is sugarcane

Atrazine

Atrazine

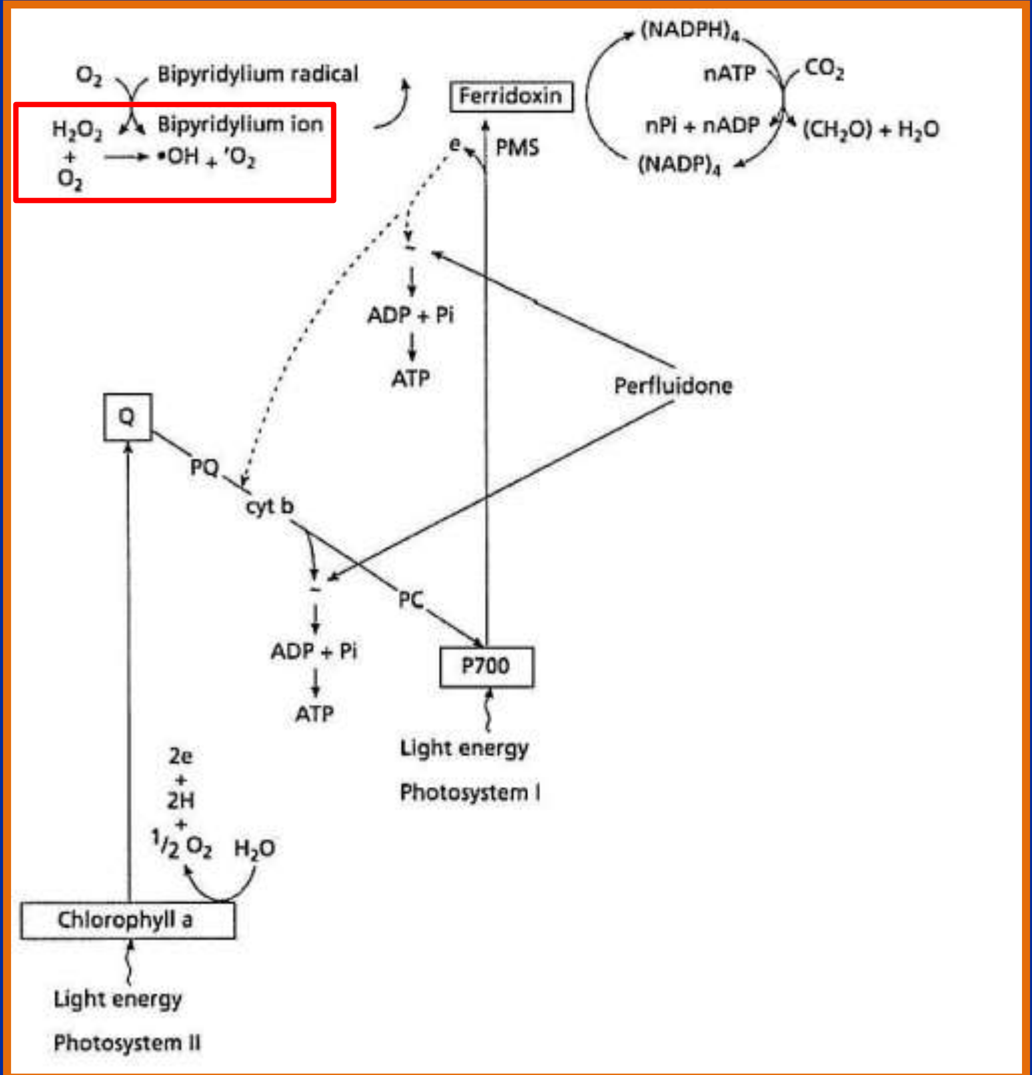
Resistance Concerns in SE U.S.

- Common groundsel: Washington (1970)
- Basis of resistance: triazines did not bind to the QB protein in resistant variants
- Several resistance cases have appeared in the SE US since 1976 – pigweeds, lambsquarters
- No resistance issues in Florida
- Most resistance has occurred in the MW US

Inhibition of Photosynthesis at Photosystem I

- Non-selective contact activity (membrane disruptors)
- Act as electron interceptors
- Result is inhibition of photosynthesis
- Membrane disruption is secondary response
- One family: bipyridyliums
- No soil activity due to strong adsorption

Inhibition of Photosynthesis at Photosystem I



Inhibition of Photosynthesis at Photosystem I: Bipyridyliums

- Examples of FL importance:
  - Paraquat
    - Nonselective for burning down vegetation
    - Major concern – acutely toxic
  - Diquat
    - Aquatic use

Inhibition of Photosynthesis at Photosystem I: Bipyridyliums

Resistance Concerns in SE U.S.

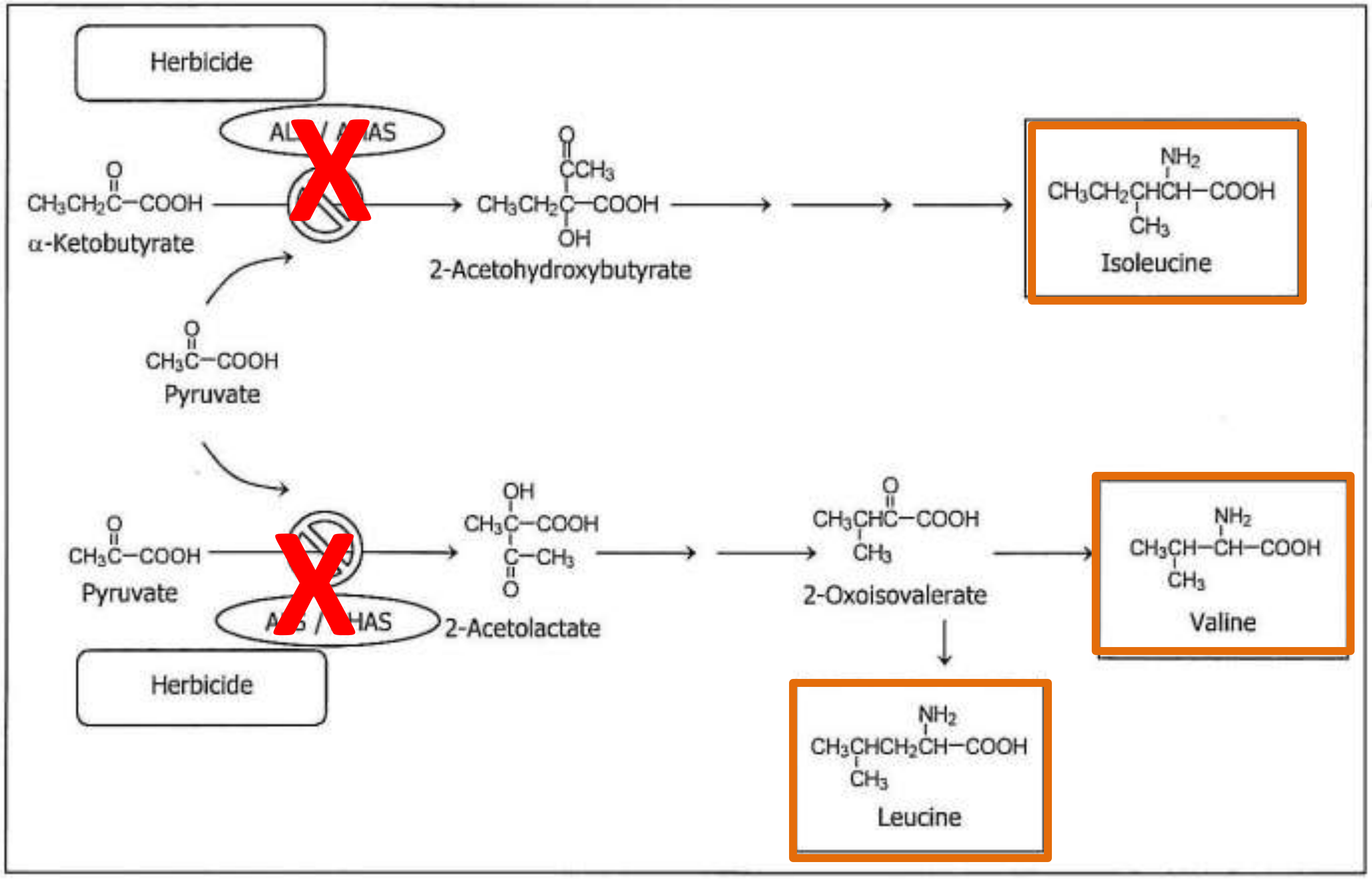
- American black nightshade: Florida (1985)
- Goosegr
- Dotted d
-

Amino Acids and Proteins Inhibition

- Acetolactate Synthase (ALS) Inhibitors
  - Amino acids: building blocks of proteins
  - Plants contain 20 different amino acids
  - ALS enzyme necessary for 3 amino acids
  - Enzymes serve as catalysts

Acetolactate Synthase (ALS) Inhibitors

- **Mode of action: inhibition of ALS**



Acetolactate Synthase (ALS) Inhibitors

- Mode of action: inhibition of ALS
  - Growth stops immediately – POST
  - Shortened internodes – PRE
  - General chlorosis
  - Some grasses:
    - Reddish-purple leaves
    - Lack of root formation
  - Purple-black leaf veins
  - Necrosis slow: 3 to 4 weeks

Acetolactate Synthase (ALS) Inhibitors

- Imidazolinones
- Sulfonylureas
- Triazolopyrimidines
- Pyrimidinyl(thio)benzoates

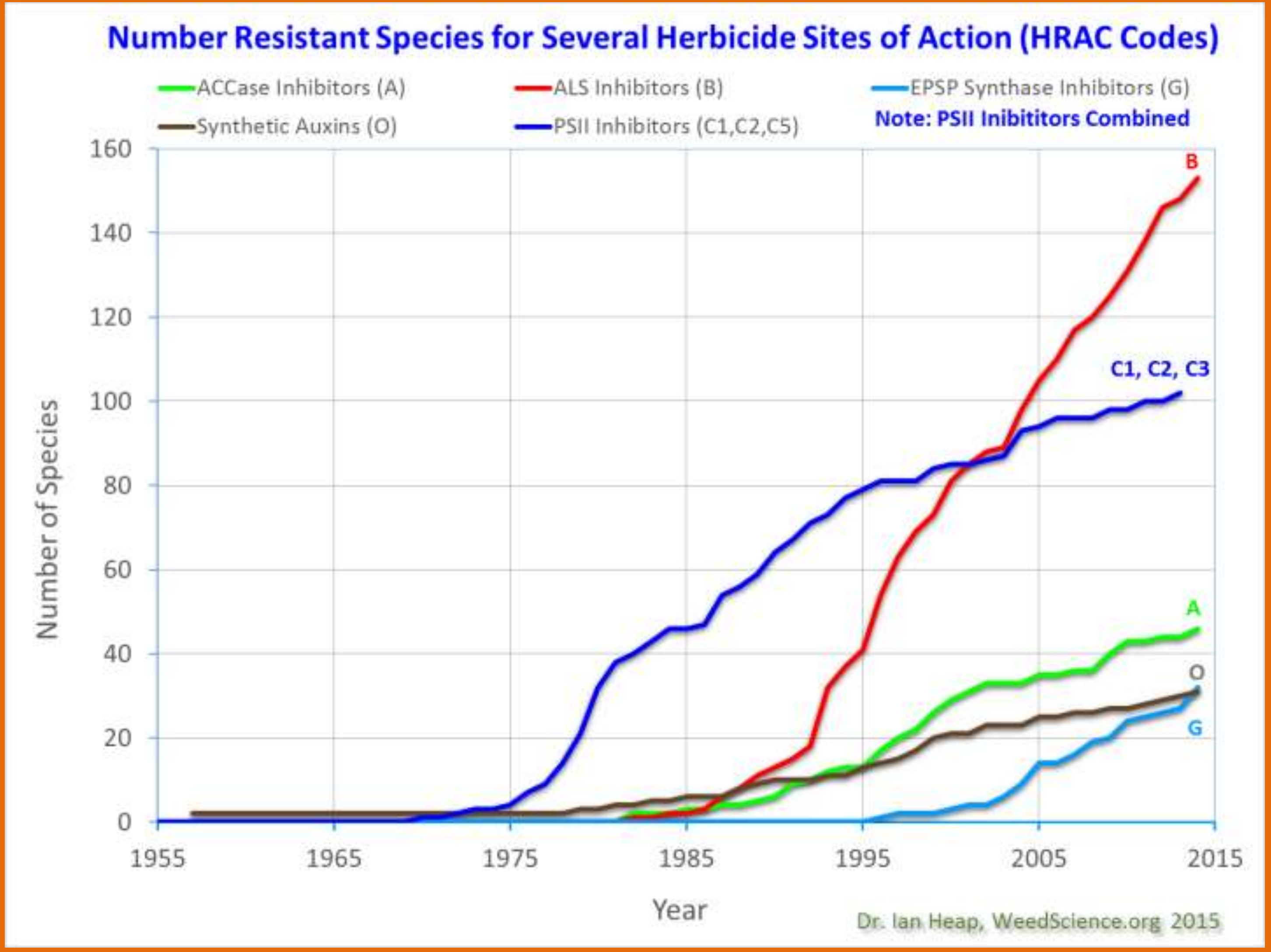
Sulfonylureas

- General characteristics
  - Wide variety of crops and non-crop sites
  - Foliar and soil activity
  - Very bioactive at extremely low rates (<0.5 oz/A)
  - Can be soil persistent (high soil pH and OM in cooler climates)
  - Very safe toxicology profile

Sulfonylureas

- Examples of FL importance:
  - First marketed in 1981
  - More than 30 registered
  - Halosulfuron
  - Chlorimuron
  - Metsulfuron (non-crop)

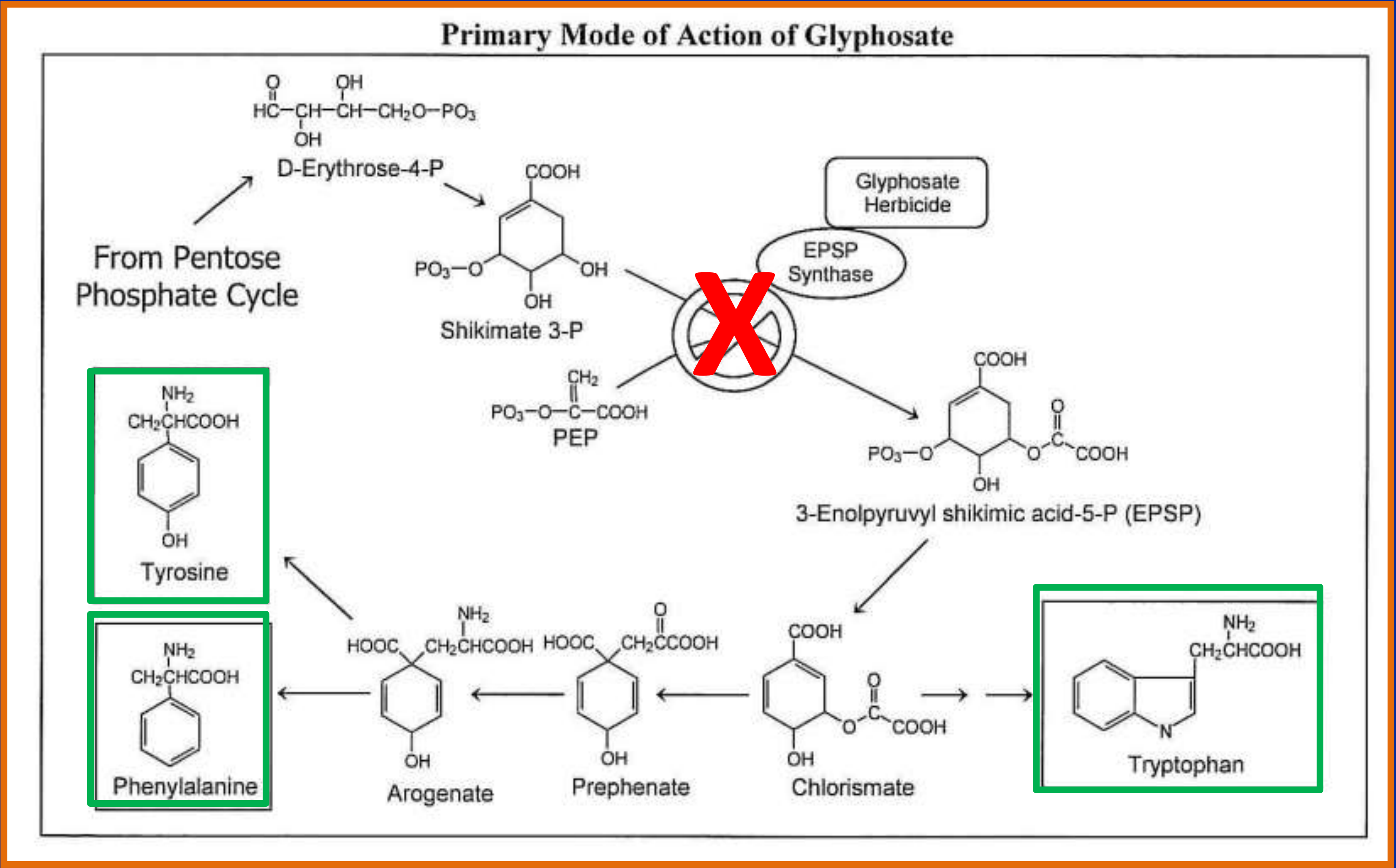
Resistance Concerns



Inhibition of EPSP Synthase

- Amino acids = protein building blocks
- 20 essential amino acids
- Glycines target EPSP synthase
- Glyphosate

Inhibition of EPSP Synthase



Inhibition of EPSP Synthase

- After glyphosate app:
- Growth immediately stops
- Broadleaves: general chlorosis, mottled
- Grasses: purpling
- Necrosis: 1 to 3 weeks
- Drift injury: growing point regions

Inhibition of EPSP Synthase: Glycines

- Examples of FL importance:
  - Glyphosate
  - Ideal qualities
    - Low mammalian toxicity, rapidly degraded in soil, low cost
  - Early 1980s: First pesticide with world-wide sales of over $1 billion
  - Forms: acid, ammonium, isopropylamine, and trimesium salts
  - Controls virtually all annual and perennials, but generally is most phytotoxic to annual grasses
  - Strongly adsorbed by soil

Dissolved Minerals and Glyphosate

Water Source

- Several herbicides (including 2,4-D, dicamba, and glyphosate) have an overall negative charge
- These herbicides can be influenced by hard water cations
  - Form precipitates
  - Lower probability of passing through plant cuticle

Dissolved Minerals

Water Source

- **Water hardness: a measurement of the total amount of calcium and magnesium ions in water**

Parts per million (ppm/gal)	World Health Organization Water Classification
0 - 114	Soft
114 – 342	Moderately hard
342 – 800	Hard
> 800	Extremely hard

$Ca(NO_3)_2$ – Glyphosate Study

- Greenhouse study at University of Tennessee
- Evaluated 4 specified levels (250, 500, 750, 1,000 ppm) of mix-water hardness using $Ca(NO_3)_2$ with glyphosate
- Visual % control of 4 weed species evaluated
  - Yellow nutsedge
  - Pitted morningglory
  - Broadleaf signalgrass
  - Palmer amaranth

Mueller, et al. 2006. Weed Technol. 20:164-171.

$Ca(NO_3)_2$ – Glyphosate Study

Cation	ppm	Y. nutsedge	P. morningglory	B. signalgrass	P. amaranth
		------------------------------% control (21 DAT)------------------------------			
None	0 (soft)	76	77	98	99
Calcium	250 (m. hard)	75	76	98	99
	500 (hard)	64	66	81	89
	750 (hard)	49	56	75	81
	1,000 (e. hard)	40	37	64	78
	LSD	5	6	7	5

Study also compared 3 glyphosate salt formulations: isopropylamine, diammonium, potassium: no differences

Mueller, et al. 2006. Weed Technol. 20:164-171.

Dissolved Minerals

Water Source

- The effects of hard water can be reversed with a water conditioner - commonly ammonium sulfate
- Ad d th

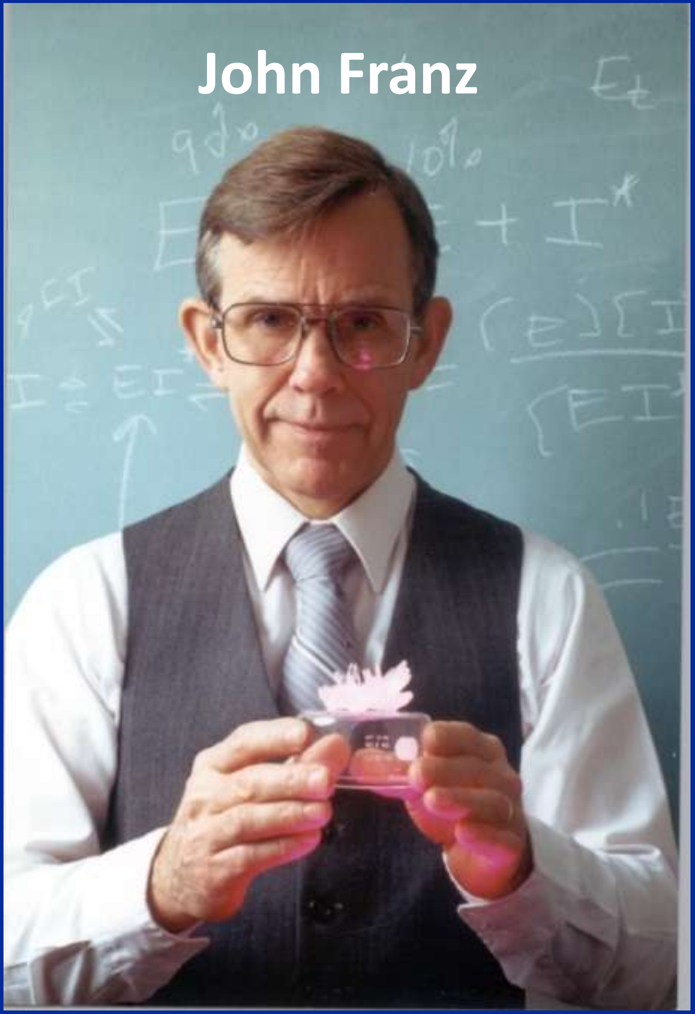
7.4 Ammonium Sulfate

The addition of 1 to 2 percent dry ammonium sulfate by weight or 8.5 to 17 pounds per 100 gallons of water may increase the performance of this product, particularly under hard water conditions, drought conditions or when tank mixed with certain residual herbicides, on annual and perennial weeds. The equivalent rate of ammonium sulfate in a liquid formulation may also be used. Ensure that dry ammonium sulfate is completely dissolved in the spray tank before adding herbicides. Thoroughly rinse the spray system with clean water after use to reduce corrosion.

History of Glyphosate

- **John Franz**
  - Organic chemist
  - Hired by Monsanto in 1955
  - Discovered glyphosate (1970)
  - Holds >800 patents

Paid $5 for discovering glyphosate – his first patent!



Inhibition of EPSP Synthase: Glycines

- Transgenic herbicide-resistant crops (worldwide)
  - Represent 10% of the total area of crops grown
  - Soybean: 60% of the plantings
  - Cotton: 30%
  - Canola: 20%
  - Corn: 15%
- U.S. is largest producer of transgenic herbicide-resistant crops followed by Argentina, Brazil, and Canada

Resistance Concerns

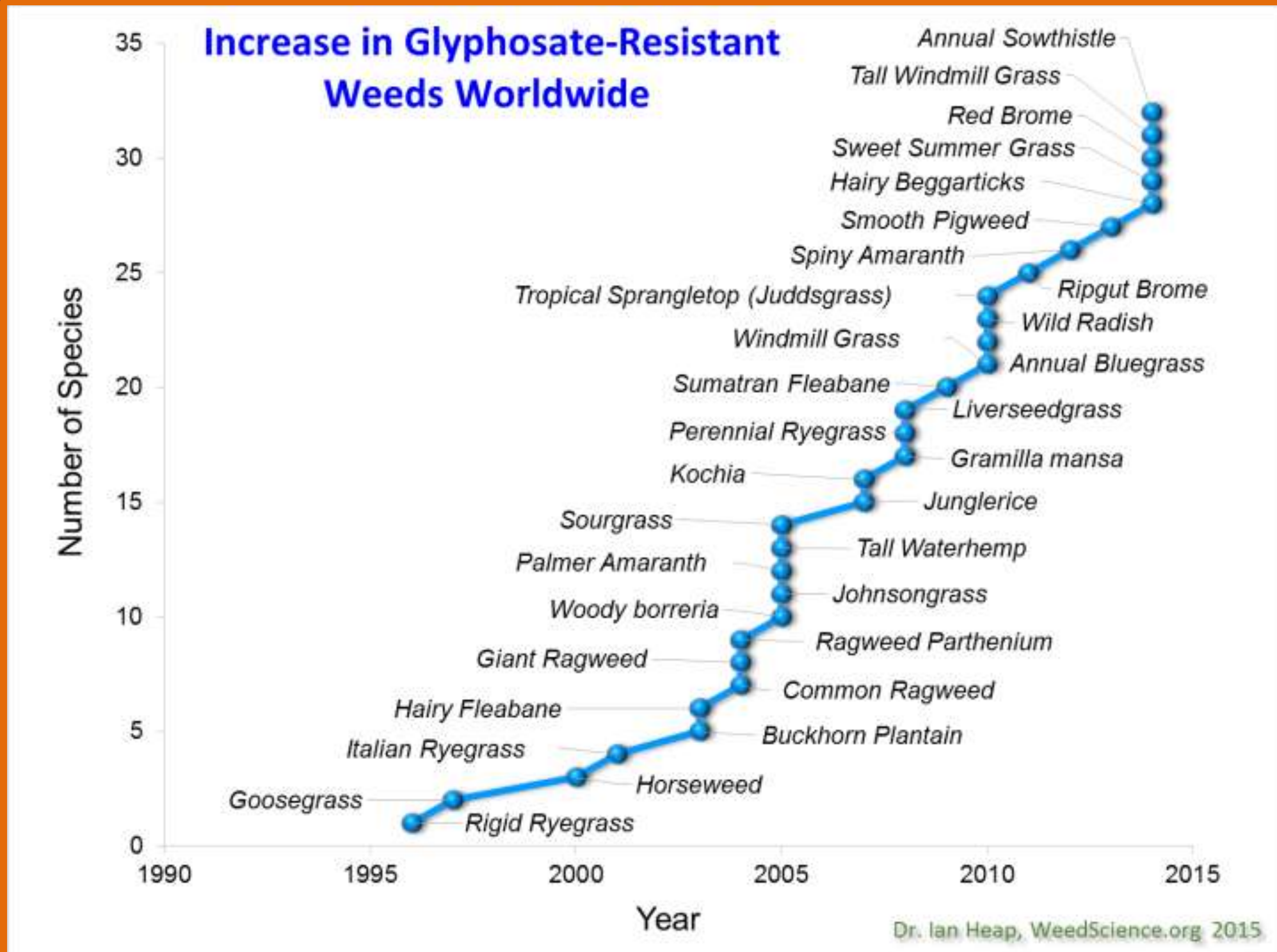
Early 1990s document:

"Because glyphosate is non-selective, Monsanto has insisted that glyphosate resistant weeds will not appear with the use of this herbicide. With the imminent release of glyphosate resistant corn and soybeans, this hypothesis will soon be tested on potentially millions of acres. Resistant weed populations have been reported already in locations outside the USA."

Resistance Concerns in SE U.S.

Weed species	Number of SE states
Palmer amaranth	11 (Florida in 2013)
Common ragweed	5
Giant ragweed	4
Horseweed	7
Italian ryegrass	5
Johnsongrass	3
Common waterhemp	2
Tall waterhemp	3
Goosegrass	2
Spiny amaranth	1
Annual bluegrass	1

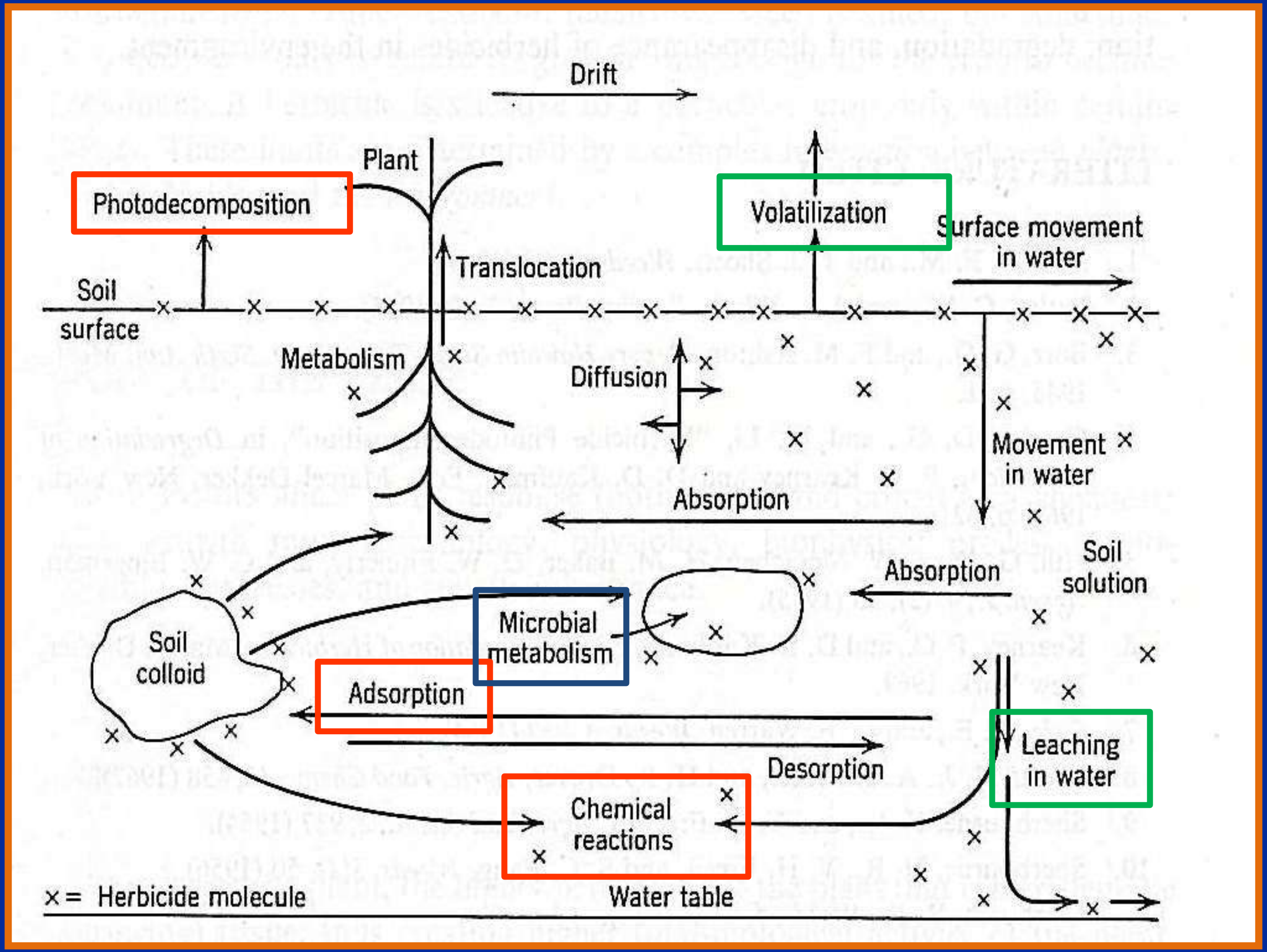
Resistance Concerns Worldwide



Where Do Herbicides Go?

- Plant uptake
- 3 general processes of herbicide in soil:
  - Chemical
  - Physical
  - Microbial

Herbicides and the Soil



Herbicides and the Soil

- Chemical processes
  - Adsorption
    - Electrical attraction forming a bond
    - Most important factor in which herbicides are unavailable in soils
    - Occurs in clay, organic matter fractions
    - More strongly adsorbed in dry soils - displaced readily from clay by water
    - Organic matter most important factor
    - Greater in low pH soils

Herbicides and the Soil

- Chemical processes
  - Photochemical decomposition
    - Degradation due to light

Herbicides and the Soil

- Chemical processes
  - Chemical reactions with soil constituents
  - Least understood due to difficulty in obtaining a sterile soil free of microorganisms with which to work
    - Oxidation – reduction (transfer of electrons)
    - Hydrolysis (water breaks chemical bonds of molecules)
    - Formation of water-insoluble salts (soils with high Ca^{+2} content)
    - Formation of chemical complexes

Herbicides and the Soil

- **Physical processes**
  - Leaching
    - Movement in soils influenced by water flow
    - Desirable results of leaching:
      - Soil incorporation of herbicides
      - Enhancing plant-herbicide interception
      - Reduction of herbicide residues in soils
    - Undesirable results of leaching:
      - Poor weed control
      - Crop injury
      - Herbicide loss through volatility (moving herbicide to the soil surface by reverse leaching)

Herbicides and the Soil

- Physical processes
  - Volatilization
    - Process by which a substance passes from the liquid state to the gaseous state
    - Results
      - Poor weed control
      - Crop injury or desirable plant injury

Herbicides volatilize and are lost much more rapidly from moist soils

Herbicides and the Soil

- Physical processes
  - Volatilization
    - Vapor drift: movement of herbicide vapors in the atmosphere
    - Ester 2,4-D formulations

Herbicides and the Soil

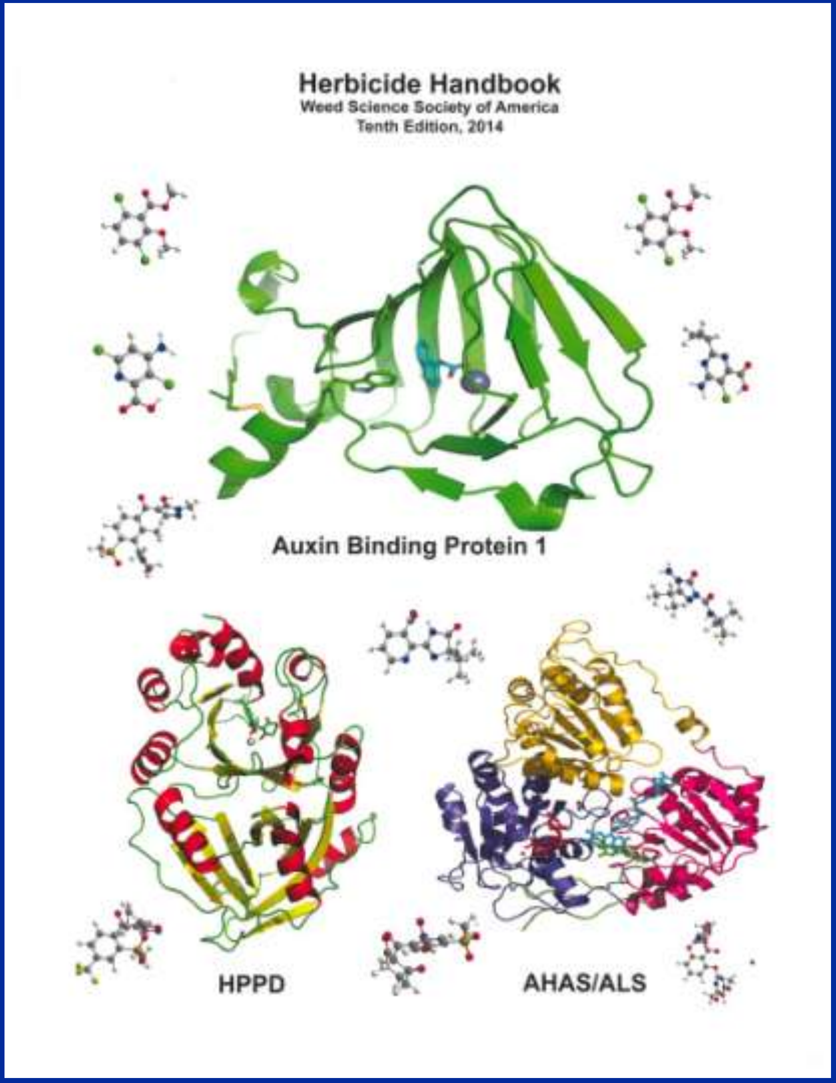
- Microbial processes
  - Decomposition (degradation)
  - Microbes attack and utilize for nutrients and energy
  - Most important means of herbicide breakdown
    - Alterations:
      - Dehalogenation
      - Dealkylation
      - Amide or ester hydrolysis
      - Beta-oxidation
      - Ring hydroxylation
      - Ring cleavage
      - Reduction of nitro groups under anaerobic conditions

Herbicides and the Soil

- Microbial processes
  - Decomposition (degradation)
    - Factors affecting:
      - Moisture (50 – 100% field capacity)
      - Aeration (well-aerated)
      - Temperature (80 – 90 degrees F)
      - Soil pH (6.5 – 8)
      - Organic matter content (Increases enhance activity)

Products formed as a result of these reactions are carbon dioxide, water, and basic elements

http://www.wssa.net/




Thanks for your attention!