Lecture

Inhibition of Photosynthesis
Inhibition at Photosystem II

1. General Information

The popular misconception is that susceptible plants treated with these herbicides "starve to death" because they can no longer photosynthesize. In actuality, the plants die long before the food reserves are depleted.

The photosynthetic inhibitors can be divided into two distinct groups, the inhibitors of Photosystem I and inhibitors of Photosystem II.

Both of these groups work in the energy production step of photosynthesis, or the light reactions. Light is required as well as photosynthesis for these herbicides to kill susceptible plants.

Herbicides that inhibit Photosystem II do not act as "electron interceptors" or "electron thieves" but rather they bind to the Q_B protein in the normal electron transport sequence, thereby blocking electron transport to the PQ pool.

Herbicides that inhibit Photosystem II are represented by several herbicide families including the symmetrical triazines, triazinones (asymmetrical triazines), substituted ureas, uracils, pyridazinones, phenyl carbamates, nitriles, benzothiadiazoles, phenyl pyridazines, and acid amides. These herbicides have preemergence and/or postemergence activity.

☞ **Note**: The pyridazinones, nitrile, and acid amide families of herbicides also have specific herbicides that do not have this mode of action (will be discussed later).

2. Mode of Action

See Figure 7.1 (The electron transport chain in photosynthesis and the sites of action of herbicides that interfere with electron transfer in this chain (Q = electron acceptor; PQ = plastoquinone; page 2). Review Photosystem I and II. The specific mode of action is as follows:

If foliar applied, herbicide moves through the cuticle into the cell and chloroplast. It binds to the Q_B protein preventing it from accepting and transferring electrons to the plastoquinone (PQ) pool in Photosystem II.

If soil applied, the herbicide moves into the root and is translocated upward in xylem. It moves into the cell and chloroplast where it binds to the Q_B protein preventing it from accepting and transferring electrons to the plastoquinone (PQ) pool in Photosystem II.

In both cases, photosynthesis is inhibited. Symptoms are too rapid to be explained by starvation. **How do we explain the symptoms of chlorosis and necrosis of leaf tissue?**

<u>chlorosis explanation</u>
electron transport blocked → excess energy transferred to chlorophyll and carotenoid pigments → chlorophyll and carotenoids destroyed by photo-oxidation (role of carotenoids is to protect chlorophyll from photo-oxidation) → result is chlorosis

<u>necrosis explanation</u>
excess energy not "quenched" by the carotenoids generates triplet chlorophyll (^{3}Chl) → interaction between triplet chlorophyll and O_2 produces singlet oxygen ($^1O_2$) radicals → membrane lipids destroyed → leakage of cell contents → desiccation of plant tissue
See Figure 6.7 (Pathway for lipid peroxidation; page 3)

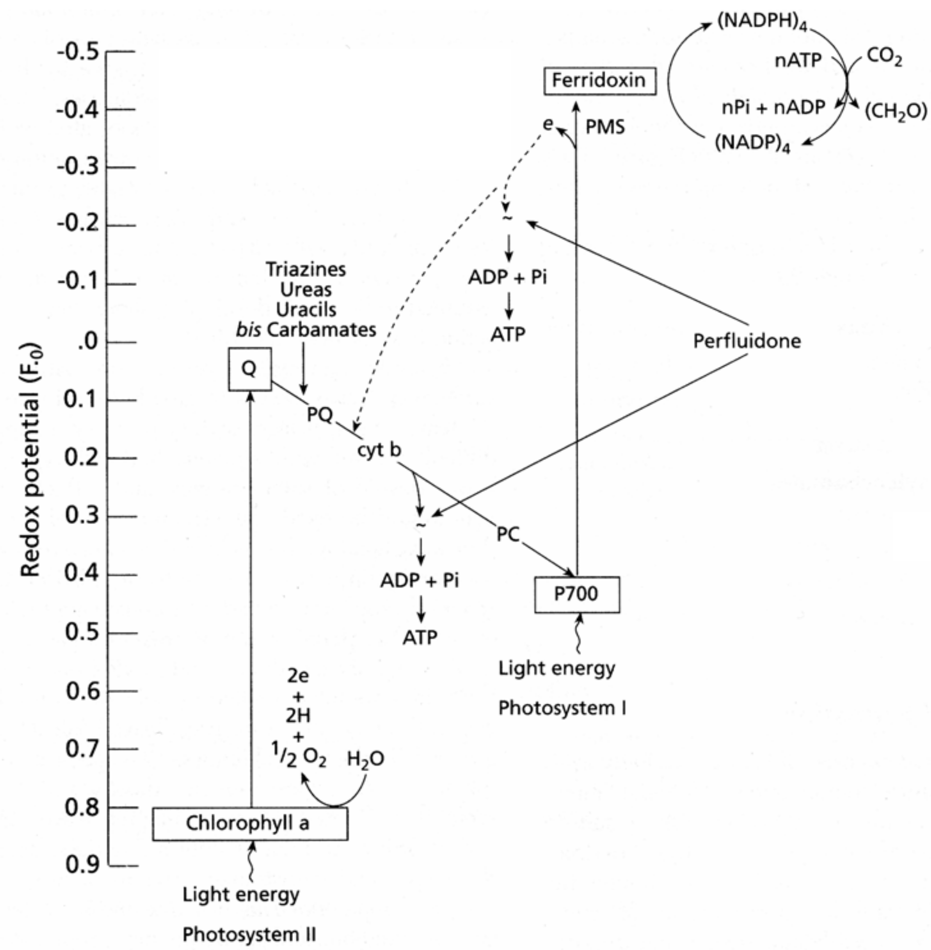
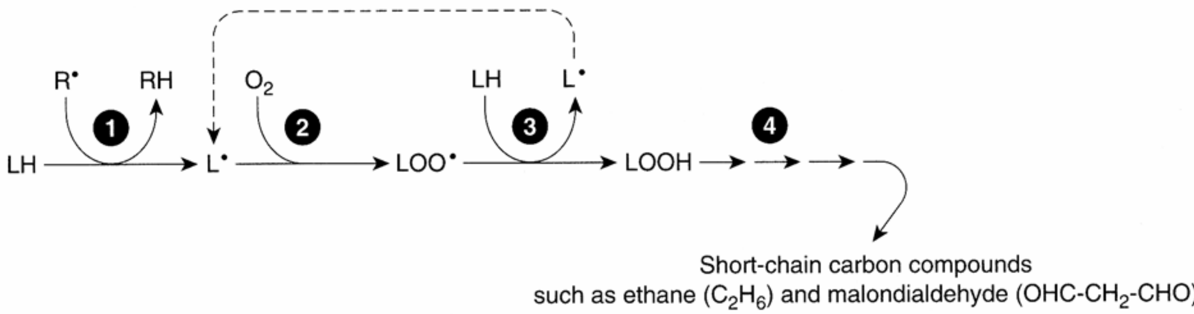


FIGURE 7.1 ■ The electron transport chain in photosynthesis and the sites of action of herbicides that in transfer in this chain (Q = electron acceptor; PG = plastoquinone).

SOURCE: F. M. Ashton and A. S. Crafts. 1981. *Mode of action of herbicides,* 2nd ed., p. 55. New York: John Wiley & Sons, Inc. Rep John Wiley & Sons, Inc.



Legend:

LH = Lipid, e.g., linoleic acid, $CH_3CH_2CH = CHCH_2CH = CHCH_2CH = CH(CH_2)_7COOH$

R• = Initiating factor (e.g., OH•, ′O_2, or ^{3}chl)

L• = Lipid radical

LOO• = Peroxidized lipid radical

LOOH = Lipid peroxide

Figure 6.7 Pathway for lipid peroxidation. Reaction of the lipid with an unstable initiating factor (1) causes oxidation of the lipid to form a lipid radical (L•). The lipid radical reacts with oxygen (2) to form a peroxidized lipid radical (LOO•). This series of reactions is perpetuated by the interaction of the peroxidized lipid radical with an unaltered lipid (3), which now become converted to a lipid radical and can feed back into the series of reactions at step (2). The other product of reaction (3) is a lipid peroxide (LOOH), which is broken down through a series of reactions (4) to alkanes, aldehydes, and other short-chain carbon compounds. This series of reactions effectively destroys the lipid components of membranes.

Source: Applied Weed Science – 2nd edition. M.A. Ross and C.A. Lembi. 1999. Prrentice Hall, NJ.

3. Site of Action

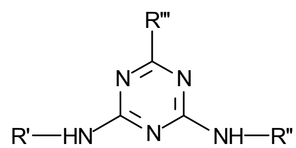
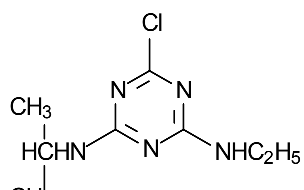
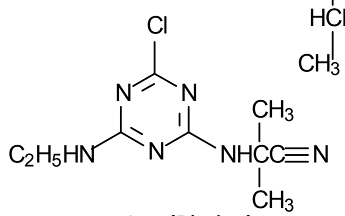
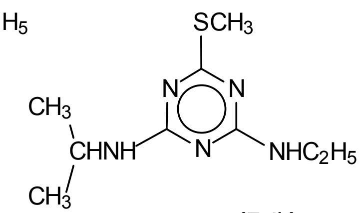
The herbicide molecule binds to one of five binding niches of the bound quinone Q_B on the chloroplast D1 thylakoid (membrane) protein. Even though herbicides in this group bind to Q_B, the specific binding sites <u>are different</u>.

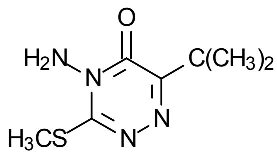
4. Symptoms

<u>root absorption</u> – herbicide symptoms will appear in lower leaves first progressing to the top of the plant and will consist of initial water soaking followed by interveinal chlorosis (veins remain green) with necrosis of leaf tips and margins. In many cases one will never see the weeds emerge because death would occur as soon as photosynthesis begins.

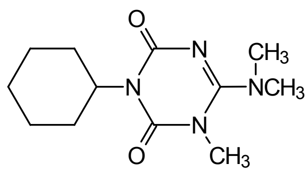
<u>foliar absorption</u> – herbicide symptoms will appear on leaves contacted by the spray. Studies indicate that little herbicide moves out of the treated leaf. Injury to that leaf will include chlorosis of leaf tips and margins followed by necrosis beginning at leaf margins and progressing toward the center. Death will occur within days.

5. Herbicide Families

Symmetrical Triazines		
Base Structure		This is a heterocyclic (more than one type of atom in a ring); ring contains 3- N's and 3-C's alternating with one another (symmetrical) This family discovered by J.R. Geigy in Basel, Switzerland in 1952; Ciba-Geigy Company; later Ciba then Novartis and now Syngenta
Examples	 atrazine (Aatrex)  cyanazine (Bladex)  ametryn (Evik)	
Others	prometon (Pramitol) prometryn (Caparol/Cotton Pro) propazine (Milo Pro) simazine (Princep)	
Metabolism	<u>plant</u>: glutathione conjugation or hydrolysis <u>soil</u>: microbial degradation half-life – cyanazine 14d; atrazine and ametryne 60 d; persistence increased by higher soil pH	
Absorption & Translocation	<u>absorption</u> by root/shoots and leaves <u>translocation</u> – if soil applied movement in apoplast to apical meristems; if foliar applied essentially no movement out of treated leaf	
Selectivity	selective - crops able to rapidly detoxify	
Herbicide Use	selective PRE and POST control of grasses and broadleafs in various crops ametryn – field corn, sweet corn, popcorn, pineapple atrazine – corn, sorghum, sugarcane, fallow, roadsides, established turf cyanazine – cotton, corn (will go off the market within the near future) weed resistance problems with 60 species resistant to atrazine worldwide; atrazine is a Restricted Use Pesticide because of groundwater concerns; efforts underway to ban atrazine; problems in mid-west (well water)	

<table>
<tr><th colspan="3">Triazinones</th></tr>
<tr><td>Example</td><td>

metribuzin (Sencor)



hexazinone (Velpar)</td><td>Both herbicides are heterocyclics with metribuzin being an asymmetrical triazine;

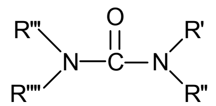
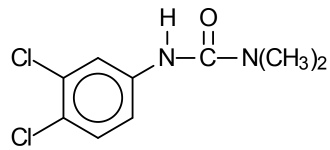
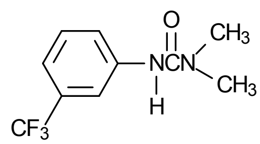
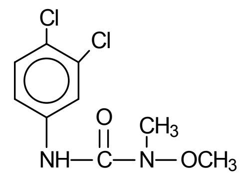
hexazinone is not a symmetrical triazine because of the double bonded O (-one designation) groups off of the ring; the “hexa” refers to the hexane ring (6-C ring attached to the N in the ring); a hexane ring contains only single bonds whereas for benzene, bonds between the 6 C’s alternate between single and double</td></tr>
<tr><td>Metabolism</td><td colspan="2"><u>plant</u>: hydroxylation, deamination, conjugation
<u>soil</u>: microbial primary means of dissipation
half-life – metribuzin 30-60 d; hexazinone 90 d</td></tr>
<tr><td>Absorption & Translocation</td><td colspan="2">readily absorbed by roots and translocated upward in xylem
when absorbed by leaves translocation to other plants parts nil</td></tr>
<tr><td>Selectivity</td><td colspan="2">selective – crops able to rapidly metabolize</td></tr>
<tr><td>Herbicide Use</td><td colspan="2"><u>metribuzin</u> controls annual broadleaf weeds and some grasses

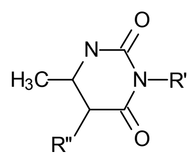
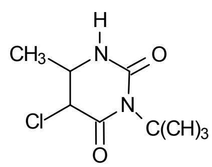
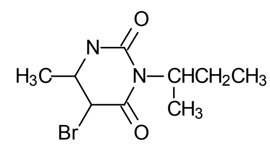
labeled for use in soybeans, potatoes, alfalfa, carrots, field corn, garbanzo beans, lentils, dry field peas, sugarcane, barley, winter wheat

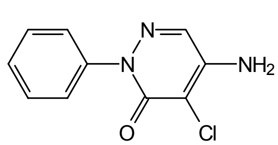
<u>hexazinone</u> controls annual and perennial grasses and broadleaf weeds

labeled for use in dormant alfalfa, pineapple, sugarcane, Christmas tree plantings, site preparation in reforestation to conifers, noncropland industrial sites, rail roads, right-of-ways; Velpar K4 (4:1 mxiture of Velpar and Karmex) labeled for use in sugarcane

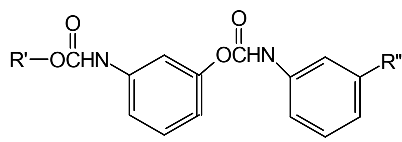
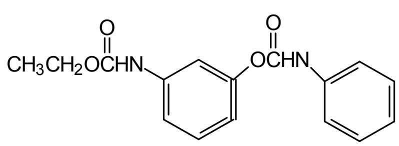
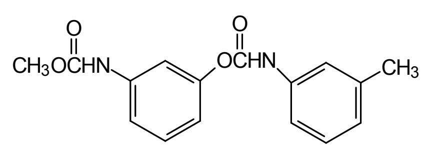
both herbicides readily leach in sandy soils low in organic matter</td></tr>
</table>

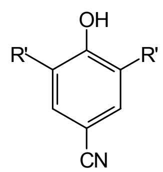
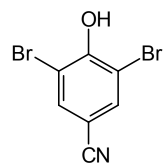
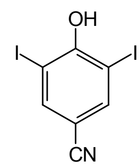
Substitued Ureas		
Base Structure		Also referred to as Phenyl Ureas. Base structure same as for the urea fertilizers; Dupont pioneered the development of this family
Examples	 diuron (Direx/Karmex)  fluometuron (Cotoran/Meturon)  linuron (Lorox/Linex)	
Others	metobromuron monolinuron siduron (Tupersan) tebuthiuron (Spike)	siduron used PRE in newly seeded zoysia turf; tebuthiuron used in pastures and rights of ways to kill trees; half life 12 to 15 months
Metabolism	<u>plant</u>: hydrolysis, conjugation <u>soil</u>: microbial primary means of dissipation half-life – diuron 90 d; fluometuron 85 d; linuron 60 d	
Absorption & Translocation	readily absorbed by roots and translocated upward in xylem when absorbed by leaves translocation to other plants parts nil	
Selectivity	selective – crop selectivity PRE primarily due to herbicide placement rather than physiological tolerance ; also differential metabolism	
Herbicide Use	these herbicides control annual broadleaf weeds and some grasses <u>diuron</u> – PRE in established alfalfa, asparagus, birdsfoot trefoil, newly sprigged bermudagrass pastures, cotton, peas, winter oats and wheat, peppermint, pecans, blueberries, cranberries, citrus, grapes, ornamental trees, peaches, pineapple; PD in artichokes, field corn, grain sorghum; POST in sugarcane <u>flometuron</u> – PPI, PRE, or POST in cotton <u>linuron</u> - PRE, PD in soybeans, corn; POST in asparagus, carrots; PRE in parsnips, potatoes	

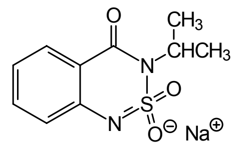
Uracils		
Base Structure		heterocyclic with two (2) N's in the 6 member ring
Examples	 terbacil (Sinbar)  bromacil (Hyvar)	
Metabolism	plant: oxidation, conjugation soil: microbial primary means of dissipation half-life – terbacil 120 d; bromacil 60 d	
Absorption & Translocation	readily absorbed by roots and translocated upward in xylem when absorbed by leaves translocation to other plants parts nil	
Selectivity	selectivity of uracils appears to be differential translocation between tolerant and susceptible plants and herbicide placement relative to plant roots and foliage	
Herbicide Use	terbacil – controls annual grass and broadleaf weeds PRE/POST in mint, pecans; POST in dormant alfalfa; PRE in sugarcane, tree fruits bromacil – controls annual and perennial grasses, sedges, and broadleafs PRE in citrus, noncropland, railroad right-of-ways, industrial sites; tell fence post story comment - both herbicides weakly adsorbed to soil colloids and leaching can be a problem; avoid drip zones of trees	

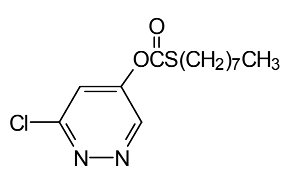
Pyridazinones		
Example	 pyrazon (Pyramin)	phenyl ring bonded to the 2- position of a pyridazinone ring (a 6 member ring with 2 adjacent N's at the 1- and 2-positions); C's at the other 4 positions of the ring and an O bonded to the C at the 3-position; another pyridazinone, norflurazon (Zorial/Solicam) inhibits carotenoid biosynthesis

Metabolism	<u>plant</u>: conjugation <u>soil</u>: microbial primary means of dissipation half-life – 21 d (4 to 8 weeks of weed control depending on soil moisture and temperature)
Absorption & Translocation	readily absorbed by roots and translocated by xylem moderate absorption by foliage with little to no translocation from treated leaves
Selectivity	conjugation in tolerant crops but not in susceptible plants
Herbicide Use	controls annual broadleaf weeds PRE/early POST in sugarbeets, red table beets adsorbs highly to organic matter

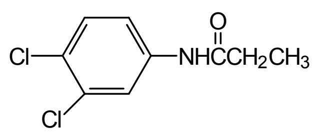
Phenyl Carbamates		
Base Structure		two phenyl rings attached to carbamic acid groups; point out the carbamic acid groups; R groups are phenyl groups
Examples	 desmedipham (Betanex)	 phenmedipham (Betanal/Spin-Aid)
Metabolism	<u>plant</u>: hydrolysis <u>soil</u>: not reported half-life – less than 1 month for each	
Absorption & Translocation	readily absorbed by foliage, but poorly translocated in phloem to other plant parts	
Selectivity	tolerant plants rapidly degrade herbicide metabolically whereas susceptible plants do not	
Herbicide Use	both herbicides provide selective POST control of annual broadleaf weeds in sugarbeets (weak on grasses) desmedipham (Betanex) is strongly adsorbed to soil and no appreciable leaching occurs Betamix is the trade name of a prepackaged combination of the two herbicides	

Nitriles		
Base Structure		base structure includes a C-N triple bond off of the benzene ring
Examples	 bromoxynil (Buctril)  ioxynil (Totril/Mate)	
Metabolism	plant: hydrolysis, decarboxylation soil: microbial primary means of dissipation half-life – approximately 7 d for each herbicide	
Absorption & Translocation	readily absorbed into leaves with little to no basipetal movement; no PRE activity	
Selectivity	selective – differential metabolism	
Herbicide Use	both herbicides control annual broadleaf weeds bromoxynil – POST in wheat, barley, oats, rye, triticale, field corn, pop corn, grain sorghum, peppermint, spearmint, onions, flax, garlic, turfgrasses ioxynil – POST in small grains, onions, poppies, rice, sugarcane, flax, pastures both herbicides considered to be contact herbicides since chlorosis occurs within hours and necrosis develops in 3 to 6 days comments: BxN cotton (bromoxynil x nitrilase); the nitrile herbicide, diclobenil (Casoron), inhibits cell wall synthesis	

Benzothiadiazoles		
Example	 bentazon (Basagran)	only one herbicide in this family; also considered to be a contact herbicide; sulfur in structure
Metabolism	plant: conjugation soil: microbial primary means of dissipation half-life –20 d with little to no soil activity	
Absorption & Translocation	absorbed by leaves with little to no translocation by photosynthate stream (symplast) rapidly transported in transpiration stream to leaves following root absorption	
Selectivity	differential metabolism	
Herbicide Use	POST control of broadleaf weeds and yellow nutsedge (does not control grasses) in soybeans, beans, peas, peanuts, corn, sorghum, rice, peppermint, spearmint; contact herbicide foliar bronzing may occur on tolerant crops such as soybean	

Phenyl Pyridazines		
Example	 pyridate (Tough)	only one herbicide in this family; also considered to be a contact herbicide
Metabolism	plant: hydrolysis followed by conjugation soil: hydrolysis by microbes half-life – 7 to 21 d with little to no soil activity	
Absorption & Translocation	rapidly absorbed by foliage, but poorly translocated	

Selectivity	not known
Herbicide Use	POST for control of annual broadleaf weeds in cabbage, field corn, peanuts, winter wheat considered to be contact herbicides since chlorosis occurs within hours and necrosis develops in 3 to 6 days

Acid Amides		
Example	 propanil (Stam/Wham EZ)	point out the amide base structure; other acid amide herbicides have a different mode of action; considered to be a contact herbicide
Metabolism	plant: hydrolysis by aryl acylamidase soil: microbial half-life – 1 d with no soil activity	
Absorption & Translocation	readily absorbed by foliage with limited movement from the treated leaf	
Selectivity	selective – aryl acylamidase activity is higher in the tolerant crop than in the susceptible weed	
Herbicide Use	propanil controls annual grass and broadleaf weeds in rice, wheat, barley considered to be contact herbicides since chlorosis occurs within hours and necrosis develops in 3 to 6 days; propanil-resistant barnyardgrass	

6. General Comments

Many of the photosynthetic inhibitors were developed in the early 1950's, but their mode of action was not determined until 1961. In the 1970's, photosynthetic inhibitors made up about 50% of all commercially available herbicides. Presently, they make up about 30% of all herbicides used.

Propanil, though included here, has other modes of action including inhibition of RNA/protein synthesis, inhibition of anthocyanin, and various effects on the plasmalemma.

In contrast to the photosynthesis inhibiting herbicides presented in this handout, the nitrile herbicide dichlobenil (Casoron) inhibits cell wall synthesis; the pyridazinone herbicide norflurazon (Zorial/Solicam) is a pigment inhibitor; the acid amide herbicide pronamide (Kerb) is a mitosis inhibitor; and the acid amides metolachlor (Dual), alachlor (Lasso), napronamide (Devrinol), and others are seedling root/shoot inhibitors.

7. References

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