Herbicide Mode of Action

Greg MacDonald
University of Florida
Chemical - Herbicides

- over 150 active ingredients registered
- over 4000 trade names
- herbicides account for 55% of pesticide use
Names on the Label

- **Trade name** - marketing; lives with the life of the product
- **Common name** - active ingredient(s)
- **Chemical name** – IUPAC approved name, internationally recognized
Herbicide History

- Carthage - 100 B.C. (salted the ground)
- Copper $\text{SO}_4$, sulfuric acid, salts - late 1800s
- Petroleum oils, Stoddard’s Solvent - 1900’s
- 2,4,6-dinitrophenol - 1932
- 2,4-D - 1944
Herbicides

• Herbicide is a chemical compound, generally organic, that is used to control plants.

• **Chemistry of the herbicide dictates** -
  – how it works in the plant
  – how it behaves in the environment
  – how it can be stored, mixed and applied
Application Methods

- pre-plant, pre-plant incorporated, preemergence
- at-cracking, early postemergence
- mid-post, late post, layby, salvage
- post-directed, shielded sprays, ropewick
Application Methods

- Apply to the soil or water - taken by plant roots or seedlings
- Apply to the leaves, bark, stem
- contact herbicides - only what they hit
- systemic herbicides - throughout plant
- placement selectivity can be achieved at either level but ................................ need to know the herbicide
Formulations

- water soluble, oil soluble, salts, esters
- clay suspension, pellets, granules, wettable powders, emusifiable concentrates
- the goal of the formulation is to: store, mix/spray in water, get it in the plant, and minimize off-target damage
Persistence/Environmental Fate

- Factors affecting herbicide persistence in the environment:
  - physical processes
  - chemical processes
  - biological processes
Persistence/Environmental Fate

- Physical Processes - VOLATILITY
  - temperature, soil moisture & composition
  - as temperature increases, volatilization increases
  - generally less volatilization in moist soil, but can have volatilization in wet, heavy soils
  - less volatilization in heavier soils w/ high OM
Persistence/Environmental Fate

• Physical Processes - LEACHING
  – most movement is downward, but can be upward (capillary flow)
  – affected by: soil texture, colloidal adsorption, water solubility of herbicide, chemical charge
  – more leaching in sandy soils with low OM

• Physical Processes - EROSION
  – runoff where the herbicide moves with the soil
Persistence/Environmental Fate

- physical processes -
  - volatility - hot and windy ↑
  - leaching - sandy soils, high rain ↑
  - erosion - high rain in short time ↑
Persistence/Environmental Fate

- Chemical Processes - ADSORPTION
  - herbicides poorly adsorbed to sand, silt
  - highly adsorbed to clays and organic matter
  - reduces the amount herbicide available to plants, slows leaching, retards breakdown
  - greatly influenced by soil pH (pKa’s, charges)
Persistence/Environmental Fate

- Chemical Processes - Photodecomposition
  - degradation by sunlight (generally UV light)
- Chemical Processes - HYDROLYSIS
  - molecules in the soil or water chemically react with the herbicide, breaking the herbicide down
Persistence/Environmental Fate

- chemical processes
  - adsorption - sandy soils, variable pH ↓
  - photodecomposition - high light ↑
  - hydrolysis
Persistence/Environmental Fate

• Biological Processes - MICROBIAL
  – microbes use the herbicide as a food source
  – generally a favorable process, but can be detrimental (breakdown too quickly - lose weed control)
  – soil temperature, aeration, pH, moisture affect microbial activity and herbicide breakdown

• Biological Processes - DETOXIFICATION
Persistence/Environmental Fate

- biological processes
  - microbial - high temp., humidity ↑
  - detoxification
Herbicides - Background

• grouped according to chemical family (structure) - generally relates to activity, but not always...........somewhat confusing

• can also be grouped by how they work to control plants (mode of action) – this is how herbicides will be classified and explained in this class
How herbicides work

• Controlled/selective plant poisoning
  – applied to soil (root uptake) and/or leaves
  – contact or systemic
  – selective vs. non-selective

• each herbicide has unique properties, some more environmentally friendly
Mode vs. Mechanism

- **mode-of-action** -- symptoms that occur after herbicide application leading to plant death
- **mechanism-of-action** -- actual biochemical site of herbicide activity
  - generally enzyme or co-factor
  - in some cases actual ‘site’ is unknown
More Detailed Symptomology

- contact vs. systemic herbicides
  - contact herbicides only affect what they hit
  - systemic herbicides move throughout the plant
- some systemic herbicides only move up from the roots to the leaves in the water stream
- other systemic herbicides move both up and down, track to areas of growth
Herbicide/Plant Interactions

- **Selectivity** – differences in the response differing plant species to a herbicide
  - Placement – crop does not take up the herbicide while the weeds do.
    - Time – before the crop emerges
    - Spatial – located away from crop (hooded sprayer)
  - Differential uptake – crop takes up less herbicide
  - Metabolism – plant breaks down herbicide via oxidation, dehydroxylation, reduction
    - Glutathione or amino acid conjugation
    - Sequestration in vacuole
  - Differential binding at the enzyme level – the herbicide binds to the weed enzyme but not the crop enzyme
Herbicide Selectivity

- **placement** - keep it away from desirable plant
- **uptake** - apply so it doesn’t get in and move
- **metabolism** - some plants breakdown herbicides but.... ...
- **target site** is different
Mechanisms of Tolerance

Herbicide X
not absorbed

Sequestered in vacuole

X does not binds to enzyme Y

X metabolized to Z
Plant Processes

1. photosynthesis
2. amino acids and proteins
3. fatty acid synthesis
4. growth inhibition
5. cell membranes
6. pigment synthesis
7. growth regulation
1. Photosynthesis

- process where the plant uses light energy to convert $\text{CO}_2$ and $\text{H}_2\text{O}$ to sugars, release $\text{O}_2$

- Light reactions
  - chlorophyll absorbs light
  - passes energy down a biochemical chain
  - form intermediates to drive sugar formation
Z-scheme

Photosystem II

Chl

redox chain

Photosystem I

Chl

Fd Bnd

Fd Sol

NADP^+ + H^+ → NADPH + H^+

energy of molecules

H_2O → O_2 + 4H^+ + 4e^- + 2H^+

ADP + Pi → ATP

photon

photon
Herbicides - Photosynthesis

- block the flow of energy from chlorophyll to the intermediates
  - plant cannot make sugars - starves
  - chlorophyll continues to absorb light and this ‘excess’ energy forms toxic intermediates
- generally soil active, root uptake and movement through water stream to leaves
Substituted Ureas

- **Diuron (Karmex), tebuthiuron (Spike)**
- used in a variety of cropping systems for broadleaf and some grass control
- mostly soil applied, but some foliar activity
- root uptake, translocation via water stream, little movement from foliar applications
- potent inhibitors of photosynthesis
Triazines

- atrazine, prometon (Pramitol)
- wide variety of crops - corn, fruits, beans...and noncropland areas.
- mostly soil applied, but some foliar activity
- root uptake, translocation via water stream, little movement from foliar applications
- potent inhibitors of photosynthesis
Uracils

- *bromacil and terbacil (Sinbar)*
- noncropland, fruit and nuts, some forage
- mostly soil applied, but some foliar activity
- root uptake, translocation via water stream, little movement from foliar applications
- potent inhibitors of photosynthesis
Benzonitriles

- *bromoxynil* - POST in corn, BXN cotton
- primarily broadleaf control, contact activity
- inhibits photosynthesis
- *dichlobenil* - PRE in ornamentals, fruit, aquatics (grass, sedge, some BL activity)
- causes severe stunting, blocks cell plate formation in dividing cells
Carbamates

- desmedipham & phenmedipham - POST
- BL weed control in sugar beets and veggies
- inhibit photosynthesis
- asulam - POST BL and grass weed control in certain turf, sugarcane, alfalfa and flax
- mitotic inhibitor, prevents cell division
Bentazon

- used postemergence in corn, soybeans, rice, and several veggies for BL weeds and yellow nutsedge control
- little movement within the plant, contact activity
- inhibits photosynthesis
Photosynthesis – Symptoms
Photosynthesis – Symptoms
2. Amino acids and Proteins

- essential building blocks for plant growth and function
- unlike animals, plants make their own
- amino acids are the primary components of proteins and nucleic acids
- proteins are generally storage proteins or enzymes
Herbicides - Amino Acids

- generally target a specific enzyme
  - blocks a vital step in the formation of amino acids—proteins, enzymes...
  - aromatic amino acids
  - branched chain amino acids
- dependent on plant growth for activity
  - better growth - better control, slow death
- systemic herbicides, some have soil activity
Imidazolinones

- **Imazapyr (Arsenal, Habitat), imazapic (Plateau)** - crops & vegetation management
- foliar & soil activity, used PPI, PRE or POST (soil activity can cause persistence)
- grasses, BL’s and good nutsedge activity
- accumulates in meristematic regions
- inhibit the synthesis of the amino acids valine, leucine, and isoleucine
Sulfonylureas

- several herbicides - low use rates, selectivity (*Oust, Escort*)
- wide variety of crops & non-crop situations
- PRE or POST - broadleaf, grass and sedges
- rapidly absorbed by roots, foliage - translocated throughout the plant and accumulates in meristematic regions
- inhibit the synthesis of the amino acids valine, leucine, and isoleucine
Sulfonanilides

- **chloransulam, flumetsulam, diclosulam**
- PRE broadleaf weed control in corn, soybeans, peanuts, some POST activity
- rapidly absorbed by roots, foliage - translocated throughout the plant and accumulates in meristematic regions
- inhibit the synthesis of the amino acids valine, leucine, and isoleucine
Pyrithiobac

- labeled for PRE and POST use in cotton
- broadleaf weed control - pigweeds, MG’s
- rapidly absorbed by roots, foliage - translocated throughout the plant and accumulates in meristematic regions
- inhibit the synthesis of the amino acids valine, leucine, and isoleucine
Glufosinate - *Finale*

- postemergence broadspectrum material
- labeled for no-till, noncrop, and certain fruit and nut crops
- foliar uptake with limited translocation
- blocks the incorporation of nitrogen in amino acids - causes the buildup of toxic levels of ammonium
glufosinate

Entireleaf morningglory

Corn
glufosinate

Tomato

Soybean
Glyphosate - *Roundup*...etc.

- broadspectrum postemergence weed control
- glyphosate labeled in multitude of areas
- For use in Roundup-Ready crops
- extensively translocated throughout the plant, extremely stable in plant
- blocks synthesis of aromatic amino acids
glyphosate
glyphosate

Entireleaf morningglory
Glyphosate injury on pecans
3. Fatty Acid Synthesis

- Fatty acids are the primary building components of cell membranes and many intercellular membranes
- Inhibition of fatty acids results in stunted growth and eventually death due to lack of membranes for cellular integrity
Aryl-oxy-Phenoxyxs & Cyclohexadiones

- *Fusilade, Select, Assure II, Poast*
- registered in several crops, noncropland
- grass activity only, postemergence
- translocated to growing portions
- inhibits fatty acid synthesis, slow death
Select/Fusilade

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Corn
Amides/Chloroacetamidess

- *Metolachlor (Dual), pronamide (Devrinol)*
- used PPI or PRE in several crops, control grasses & certain broadleaves
- inhibit root and shoot growth through the inhibition of long chain fatty acid synthesis
Thiocarbamates

- *EPTC, metam, etc.*
- nearly exclusively PPI due to volatility
- several crops - corn, rice, beans, non-crop
- mainly grasses, but some sedge and BL’s
- root and shoot absorbed - germinating seeds
- inhibition of gibberellin plant hormone and fatty acid synthesis
4. Growth Inhibition

- plants grow by making new cells
  - process of cell division, mitosis
- plants are particularly susceptible as emerging seedlings
  - both shoot and roots
- newly forming roots can be susceptible at most stages of plant growth
Herbicides - Growth Inhibition

- most growth inhibition herbicides are soil applied and generally affect seedling weeds
- most interfere w/ mitosis (mitotic poisons)
- soil active, little movement once absorbed
Dinitroanalines

- ethalfluralin, trifluralin (*Treflan*)
- *Pendimethalin* (*Prowl*), *oryzalin* (*Surflan*)
- soil applied, PPI or PRE - annual grasses and certain broadleaf weeds
- vary in volatility and photodegradation
- prevent both root and shoot growth, inhibit cell division (mitosis)
Dichlobenil and Isoxaben

- **dichlobenil** - PRE in ornamentals, fruit (grass, sedge, some BL activity)
- causes severe stunting, blocks cell plate formation in dividing cells
- **isoxaben** – PRE in ornamentals, fruit, others (grass, some BL activity)
- causes severe stunting, blocks cell wall formation in dividing cells
5. Cell Membranes

• maintain cell integrity
  – keep things in & out

• generate electrochemical gradients
  – allows for energy production

• maintain cell structure
  – turgor pressure maintains plant structure and helps the plant grow
Herbicides - Cell Membranes

- divert normal energy flow to form toxic intermediates
  - interact with membrane and cause disruption
- cause the membrane to become “leaky”
  - gradients cannot be formed, no energy for cellular functions - endothall
- generally contact, little movement in plant
Organic Arsenicals

- **MSMA, DSMA, cacodylic acid, CMA**
- used postemergence in cotton, turf
- no soil activity
- readily absorbed by leaves, translocated to growing tips
- chlorosis, stunting, dessication
- interferes with energy transfer, enzymes
MSMA

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Corn
Bipyridylliums

- paraquat (Gramoxone) and diquat (Reward) - several registrations
- non-selective postemergence activity
- little translocation, contact
- diverts normal electron flow, causes formation of radical oxygen and cell membrane disruption
- no soil activity
PPO inhibitors

- **Flumioxazin (Valor), Sulfentrazone (Spartan) & Carfentrazone (Stingray)**
- applied POST for BL weed control
- contact, no translocation in foliar treatments
- xylem movement from soil active
- increase of light absorbing intermediates
- formation of highly toxic free radicals
Copper (Chelates, CuSO4)

- Used for algae and submersed plant control in aquatic situations
- CuSO4 more active, limited uses due to fish problems
- Appears to disrupt cell membranes, but exact mechanism is unknown
fomesafen

Tomato

Ivyleaf morningglory
6. Pigment Synthesis

- absorb light energy for photosynthesis
- also protect plant from excess light
- types of pigments
  - chlorophyll
  - carotenoids
  - flavenoids
  - anthocyanins
Herbicides- Pigment Synthesis

- block the formation of chlorophyll
- block the formation of carotenoids
  - carotenoids accept excess energy
  - when absent, chlorophyll dissintegrates
- generally slow death, plant starves
- soil active, movement through water stream
Clomazone

- clomazone labeled for use PPI (volatile) in soybeans, tobacco, cotton certain veggies
- effective on grasses and certain BL’s
- root absorbed, bleaching of leaf tissue
- inhibits chlorophyll synthesis
Pyridazinones

- **fluridone (Sonar)** labeled for aquatic weed control
- **norflurazon (Solicam)** labeled PRE in cotton, beans, peanuts, fruit/nut crops - BL’s and grasses
- root absorbed, translocated in water stream to growing points - bleaching of leaf tissue
- inhibit the synthesis of carotenoids (protective plant pigments)
Other Pigment Inhibitors

- Mesotrione and isoxaflutole
- Used pre-emergence and post-emergence in corn for grass and broadleaf control
- Blocks the formation of a precursor needed for carotenoid synthesis
- Similar mode of action to the pyridazinones, but different mechanism
Pigment Injury Symptoms
Growth Regulation

- Hormones control plant growth and developmental changes, always present.
- Grouped into 5 types - but highly interactive:
  - Auxins (light responses, apical dominance)
  - Gibberelins (elongation, flowering)
  - Cytokinins (growth, development)
  - Abscisic acid (leaf senescence, propagule form.)
  - Ethylene (leaf senescence, counteract auxin)
Herbicides - Growth Regulation

- auxin mimics - cause uncontrolled growth
  - auxin transport inhibitors
  - prevent the normal distribution of auxin
- indirectly, all herbicides can be regulators
  - Sonar (fluridone) blocks abscisic acid
  - glyphosate inhibits auxin regulation
- soil and foliar applied, systemic throughout
Benzoic Acids

• *dicamba (Banvel, Clarity)*- registered for use in corn, turf, pastures (broadleaf weed control)
• postemergence but possesses some soil activity (can be used preemergence in corn)
• readily translocated to growing tips
• interferes with RNA, DNA and protein synthesis - leading to rapid, uncontrolled growth (similar to phenoxyys)
dicamba

Hemp Sesbania

Cucumber
dicamba

Cotton

Tomato
Phenoxys

- **2,4-D, 2,4-DB, 2,4-DP, MCPA**
- BL weed control for a variety of crops (corn, pastures, legumes) and noncropland
- salt, ester and oil formulations
- foliar & root uptake- extensive translocation
- cells undergo rapid uncontrolled division and elongation
Picolinic acids

- *Triclopyr (Garlon), chlorpyralid (Transline), aminopyralid (Milestone)*
- used POST for BL weed control, brush & woody
- similar to phenoxyxs, primarily foliar applied but picloram has tremendous soil activity
- foliar & root uptake- extensive translocation
- cells undergo rapid uncontrolled division and elongation
triclopyr

Cucumber

Redroot pigweed
Diflufenzopyr

- labeled for POST use in corn, pasture/noncropland
- activity on broadleaves and grasses
- foliar and root absorbed, translocated to growing regions
- mode of action not fully understood - appears to interfere with hormonal balance