Herbicides and Fungicides

Herbicides: Phytotoxicity

- Must be able to inhibit a vital process so plants cannot grow or survive
- Because weeds grow among target plants, selectivity is important

Mode of Entry

- 1) Foliar Penetration
  - Main protection of leaf is cuticle (lipophilic)
  - Secondary protection is cell wall made of cellulose (hydrophilic)
  - Therefore, foliar herbicides must be both aqueous and lipoidal
Polar entry route
Non-polar entry route

Cuticular wax
Cutin
Pectin
Cellulose
Plasmodesmata
Plasma membrane
Cytoplasm

Cell wall
Protoplasm

Fig. 24

Effect of Surfactants

Droplet Without Surfactant
Wax Layer
Cuticle Proper
Pectin Layer
Primary Wall
Secondary Wall
Plasm Membrane
Cytoplasm

ERSP Synthase

Mode of Entry

2) Root uptake
- Herbicides applied to soil can also penetrate seeds
- If to be taken up by roots, must be able to pass endodermis (lignin or suberin coated ring of cells)
Mode of Entry

3) Stem uptake
- Little use for herbaceous weeds, good for woody plants
- Water-soluble solution must be injected or mechanically penetrate bark
- Oil-based sprays may penetrate bark but must be applied in high concentrations (enter through pores in bark)

Translocation within plant

- Symplast: total mass of living cells in a plant
- Apoplast: the non-living cell wall continuum that surrounds the symplast.

Translocation Within Plants

1) Symplastic movement:
- Protoplasm of plants is more or less continuous because of plasmodesmata and connectedness of transport cells (e.g. sieve-tube)
Translocation Within Plants

- 2) Apoplastic movement:
  - Includes cell walls, intercellular spaces and xylem elements
  - Permeable to water and dissolved solutes
  - Rate of water transport is great (>1 gallon/day for sunflower)
- Limitation: xylem moves upwards, therefore not good for foliar pesticides

Toxic Effects on Plants

- 1) Contact Toxicity
  - Kill quickly
  - Translocation often not possible in time
  - Usually act by destroying cell membranes by breaking bonds between membrane proteins and plasma membrane
  - Causes necrosis in all exposed tissues in a few days
  - Because translocation limited, plants may regrow from roots and buds

- 2) Mitotic Inhibitors
  - Inhibit growth by blocking some stage of mitosis
  - Plant growth occurs principally in meristematic regions (root/shoot tips, young leaves, buds, vascular cambium)
  - Often applied to soil to act on roots or germinating seedlings
Toxic Effects on Plants

3) Photosynthetic Inhibitors
   - Majority of herbicides
   - Because affects photosynthesis, often of little toxicity to animals

4) Respiration Inhibitors and uncouplers
   - Fig. 39

5) Nucleic acid metabolism and protein synthesis disruption
   - Many ways to have these effects
   - e.g. enter nucleus and remove histones
   - e.g. could stimulate RNA polymerase in cytoplasm
Categories of Herbicides

- A) Synthetic auxins (plant growth regulators)
- Mode of Action
  - At low doses, act as IAA mimics (auxin) & stimulates growth
  - Plants cannot degrade synthetic IAA, therefore toxic at higher doses & inhibits growth
  - Mobile by symplastic transport
  - Stimulates growth within stems, thus choking vascular tissues

Categories of Herbicides

- A) Phenoxy Alkanoic Acids (2,4-D)
  - More persistent in soil than 2,4-D
    - Degradation takes months to years
  - LD₅₀ to animals is moderate (400-500mg/kg acute oral)
  - Agent Orange in Vietnam (1965-1970) has left TCDD contamination 40yrs later
    - www.hatfieldgroup.com

Categories of Herbicides

- A) Phenoxy Alkanoic Acids (2,4,5-T)
  - Not persistent in soil
    - Rapidly degraded by soil microbes to carbon food source
  - Non-target effects include desirable plants
  - LD₅₀ to animals is low (300-1000 mg/kg acute oral)
  - Bioaccumulation potential is low
    - Most studies report complete elimination in urine by 24hrs (however, has been linked to endocrine disruption and cancer development by epidemiological studies)

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**Categories of Herbicides**

- **B) Triazines**
  - Heterocyclic nitrogen compounds
  - R-groups differ but often include chlorine
  - 2nd most important herbicides discovered
  - Quite persistent and resist degradation

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**Categories of Herbicides**

- **B) Triazines**
  - Most important is Atrazine
    - Others include simazine, propazine, cyanazine etc...
    - Atrazine especially useful in corn
  - 3 applications:
    - Preplant: remove surface vegetation
    - Pre-emergence: remove germinating broadleaves
    - Post-emergence: weed thinning

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**Categories of Herbicides**

- **B) Triazines**
  - Mode of action
    - Enters by roots, translocated by xylem
    - Ultimate site of action is chloroplasts as inhibitor of photosystem II (cleavage of water)
    - Produces toxic free radicals in light reaction because of reduced electron transfer
  - Most grasses have high tolerance due to ability to detoxify
  - Widely used in corn crops
  - Potential for resistance if used repeatedly
    - e.g. lamb's quarter (*Chenopodium album*)
  - LD₅₀ toxicity low for animals (300 [cyanazine] - 5000 [simazine] mg/kg acute oral)
Herbicide Resistance

- Resistance is common
  - Over 200 biotypes now resistant to a herbicide
  - Caused by continuous use of same herbicide or of same mode of action over several generations
  - May occur by mutations to target site of herbicide or detoxifying ability

**Atrazine Site of Action**

- D1 protein
- Plastoquinone
- Atrazine

Herbicide Resistance

- Most common form is to triazines
  - >60 resistant biotypes
  - Resistant plants have single amino acid substitution in the D1 protein, which prevents herbicide from attaching to plastoquinone electron acceptor of PSII
  - Caused by a single nucleotide base change

*Also: resistance from genetic engineering (Round-Up ready crops)*
C) Glyphosate

- Most economically important in the world because sold with ‘Round-Up Ready’ crops
- Absorbed by foliage and readily translocated symplastically
- Non-selective, high activity
- Low persistence, degraded by soil microbes within weeks
- Advantage for reduced soil erosion, as controls weeds without tillage

Mode of Action

- Inhibitor of amino acid synthesis
- Plants produce 9/20 essential amino acids (leucine, isoleucine, histidine, valine, lysine, methionine, theonine, tryptophan and phenylalanine)
- Chemicals causing breakdown in their production may often be harmless to animals
- LD50 toxicity low in animals (4000mg/kg acute oral)
Glyphosate in the “News”

“The highest level detected was 18.74 parts per billion (ppb), which was found in a 2013 Cabernet Sauvignon from a conventional vineyard. This was more than 28 times higher than the other samples tested.”

<table>
<thead>
<tr>
<th>Crop</th>
<th>MRL</th>
</tr>
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<tbody>
<tr>
<td>Bean</td>
<td>4 ppm</td>
</tr>
<tr>
<td>Lentil</td>
<td>4 ppm</td>
</tr>
<tr>
<td>Pea</td>
<td>5 ppm</td>
</tr>
<tr>
<td>Soybean</td>
<td>20 ppm</td>
</tr>
<tr>
<td>Wheat</td>
<td>5 ppm</td>
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</tbody>
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Fungicides

- Encompasses pesticides that control all types of pathogens
  - Bacteria, nematodes, as well as fungus
- Pathogenicity is often cryptic, therefore more difficult to control than weeds or insects
- Employed mostly on vegetable, fruit and nut crops
- Mostly have low mammalian toxicity (LD<sub>50</sub> in the thousands mg/kg), low persistence, biodegradable, low solubility (transport)

Fungicide Selection

- Chosen based on the following characteristics (apart from target toxicity)
  - Remain active for long time
  - Good adhesive properties
  - Good spreading properties
  - Persistence
  - Specificity (not toxic to host plant)
  - Active against range of pathogens
- Mode of action varies
  - Respiration inhibitors, protein phosphorylation, enzyme disruption etc...
Types of Fungicides

- **a) Systemic**
  - Absorbed by the plant and distributed to all parts
  - e.g. oxathiins, benzimidazoles, pyrimidines, organophosphates, triazoles, carbamates...

- **b) Non-systemic**
  - Effect only at site of application (protection)
  - E.g. dithiocarbamates, dicarboximides, dinitriophenols, quinones, antibiotics...

**Advantage of systemics:**
- Plant continuously protected without reapplication
- May be translocated to new shoots that grow after application
- Not subjected to weathering
- No residues (aesthetics)
- Have potential to work on internal plant disease
- Minimal work-related hazards

**Disadvantage of systemics:**
- Development of resistance is common (usually just one mode of action)
- Most fungicides are fungistatic, not actually fungicidal, therefore organism can recover as pesticide dissipates
Fungicide Resistance

- Potential is high due to extremely high numbers of spores (fecundity)
  - May spread rapidly
- Often, single base mutation can lead to resistance

Questions?