**Herbicides and Fungicides**

**Herbicides: Phytoxicity**
- 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
Foliar Penetration

Polar entry route
Non-polar entry route

Cuticular wax
Cutin
Pectin
Cellulose
Plasmodesmata
Plasma membrane
Cytoplasm

Cell wall
Protoplasam

Fig. 24

Effect of Surfactants

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)

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### Translocation within plant

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

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### 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

- Complicated because a single chemical may have different effects at different doses and/or different sites of action
- Some herbicides stimulate growth in one area while inhibiting in another
  - Called Epinastic effects
  - Cause stem twisting and leaf curling
  - Plant usually dies from choking of vascular tissues

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

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)
  - 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)
Categories of Herbicides

A) Phenoxy Alkanoic Acids (2,4,5-T)
- More persistent in soil than 2,4-D
  - Degradation takes months to years
- LD$_{50}$ to animals is moderate (400-500mg/kg acute oral)
- Agent Orange in Vietnam (1965-1970) has left TCDD contamination 40yrs later
  - www.hatfieldgroup.com

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

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

Atrazine Site of Action

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
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 plastocyanine electron acceptor of PSII
  - Caused by a single nucleotide base change

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

Categories of Herbicides

- 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

Categories of Herbicides

- C) Glyphosate
  - 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 Site of Action**

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Phosphoenol pyruvate → Erythrose-4-P
↓
Shikimate
↓
Shikimate-3-P
↓
5-Enolpyruvyl shikimate-3-P
↓
5-Enolpyruvyl shikimate-3-P synthetase
↓
Chlorismate
↓
Aromatic Amino Acids
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Fig. 107

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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)

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**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…

Types of Fungicides

- **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

Types of Fungicides

- **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?