This section will cover the basics of herbicide discovery, registration and laws detailing pesticide use and regulation. It will also detail the fate of herbicides in the environment and plant/herbicide interactions.
What is a Herbicide?

- A chemical compound that is used for selective or non-selective weed control. Generally an organic compound that is the product of organic chemical synthesis.
- A herbicide is a pesticide, similar to other pesticides such as insecticides, fungicides, nematicides, etc.
Herbicide Registration

- Herbicides are developed by agrichemical/agribusiness companies. A substantial amount of money is needed for a herbicide to become registered for use.
- EPA governs all pesticide registration and requires testing in several areas before a herbicide is granted a registration.
- Costs to register a compound is highly variable, but could run as high as $100 to 150 million.
Registration Costs

1. **Discovery** – synthesis, initial screening, patents, physio-chemical properties of the molecule (changes to the chemistry that impact water solubility, metabolism, environmental fate and weed/crop selectivity). These are lab and greenhouse based studies performed in the main research facility of the company that is generally linked to the chemical division.
Registration Costs

2. **Formulation** of the product – this is also tied to chemistry but involves making the final product in a form that:

- Allows to be stored in adverse conditions
- Facilitates dispersion and application in $\text{H}_2\text{O}$
- Facilitates uptake and movement in plants
- Decreases exposure/risk to end-users
- Decreases environmental risks

- Manufacturing costs are also involved in this portion of registration costs.
3. Toxicology is the most expensive part of herbicide registration. Over 120 base studies are required by EPA for registration and include acute and long-term effects, chemical properties, effect on endangered species, persistence and fate in the environment, etc.
4. **Marketing**, sales, and other associated costs (including personnel) are also required as part of a product launch campaign. Due to the high costs of registration, many herbicides target the higher volume crops such as corn, wheat, soybeans and rice. Some compounds with great utility in a lower end market are often not pursued because the costs to get the product to market cannot be recouped.
Agencies in Herbicide Regulation

- EPA – Environmental Protection Agency
- FDA – Food and Drug Administration
- OSHA – Occupational Safety & Health Adm.
- USDA – U.S. Department of Agriculture
Laws under Authority by EPA

• Safe Drinking Water Act –
  – Prevents contamination of surface and groundwater sources
  – Establish maximum contamination limit (MCL’s)

• Clean Water Act –
  – Protects water bodies and wetlands
  – Point and non-point source pollution
Laws under Authority by EPA

- FIFRA – Federal Insecticide, Fungicide and Rodenticide Act
  - Primary pesticide law, established in 1947
  - Governs all pesticides sold or distributed
  - Section 3 label – full federal registration
  - Section 18 – emergency use label
  - Section 24c – special local needs (state issued)
  - Section 5/EUP – Experimental Use Permit
Laws under Authority by EPA

- FIFRA Labeling – control when and under what conditions pesticides are:
  - Applied
  - Mixed
  - Stored
  - Loaded or used
  - Re-entry time after application
  - Crop harvest interval
  - Disposed of properly
Federal vs. State Registration

– Although section 3 grants federal use of a product, additional approval by each state must be granted – some states go with EPA unconditionally, some state require additional testing, labeling, etc.

– This is generally governed by the state department of agriculture. This agency also has jurisdiction over section 24c labels.
Laws under Authority by EPA

- Worker Protection Standard
  - In conjunction with OSHA
  - Protects agricultural workers and pesticide handlers
  - Defines Agricultural Use Requirements
  - Establishes REI (re-entry intervals)
Laws under Authority by EPA

- Certification and Training
  - Restricted use pesticides (RUP’s), those that are deemed hazardous even when used according to label
  - Private applicators – use or supervise the use of RUP’s to produce agricultural commodities on property owned or rented by themselves or their employers
  - Commercial applicators – use or supervise the use of RUP’s on any property or any purpose
  - Public applicators – use or supervise the use of RUP’s on any public property or any public purpose
Laws under Authority by EPA

• Food Quality Protection Act (FQPA) – 1996
  – Establishes single standard for pesticide residues in raw and processed foods
  – Requires consideration of aggregate pesticide exposure (including food and drinking water)
  – Requires consideration of exposure to all other pesticides with a common mechanism of toxicity when setting allowable residue levels
  – Any food, product associated with infants is elevated to a 10X safety margin
Other Agencies

- FDA – share food safety responsibilities with EPA, assists in the setting of food tolerances
- OSHA – assists in setting worker protection standards
- USDA – as part of the 1990 Farm Bill, assists EPA in compliance with the Federal Record Keeping requirement
Components of a Herbicide Label

• A sample label was covered in lab, but you should be able to locate and understand the following items on an actual label:
  – General or restricted use
  – Trade, common and chemical name
  – EPA registration number
  – Name and address of manufacturer
  – Net contents – active and inert ingredients
  – Type of pesticide, type of formulation
  – Precautionary statement, hazards to humans, animals, environment
  – Acute, delayed and allergenic effects
  – Directions for use including application types, re-entry intervals, storage and disposal, crops, etc.
  – Worker protection guidelines
Herbicide Toxicology

- **LD$_{50}$ (mg/kg)** – lethal dose that causes death in 50% of test population
  - the lower the LD$_{50}$, the more toxic the compound – takes less to cause a problem
  - Acute oral, dermal exposure

- **LC$_{50}$ (ppm)** – concentration that will be lethal to 50% of test population
  - Inhalation, aquatic exposure

- **NOEL (mg/kg/day)** – no observable effect level
  - how long does continuous exposure/feeding not cause a problem
  - This can be measured as chronic and subchronic
  - Mutagenicity (tumors)
  - Teratogenicity, oncogenicity (reproductive problems)
**Oral LD$_{50}$ of Pesticides**

- **Trifluralin** is used pre-plant incorporated in several crops to control grasses & broadleaf weeds.
- **Paraquat** is used postemergence as a broad spectrum herbicide for use in non-crop land areas.
- **Glyphosate** is used postemergence as a broad spectrum herbicide for use in non-crop and Roundup Ready crops.
- **Aldicarb** is a systemic insecticide for the control of biting and sucking insects in many crops.
- **2,4-D** is used postemergence as a broadleaf herbicide for use in turf, pastures and certain grass crops.
- **Alachlor** is used pre-emergence in many crops for grass and broadleaf weed control.
- **Atrazine** is used pre & postemergence for broadleaf & grass control in corn, turf and sugarcane.
Herbicide Dissipation

• Most of the following information on the fate of pesticides in the environment can also be found in Bulletin SL40
  http://edis.ifas.ufl.edu/SS111
Herbicide Dissipation

1. Volatilization – change in chemical form from a liquid to a vapor
   - Often results in poor weed control and off-target injury (drift)
   - As temperature goes up, volatility increases
   - The more air movement occurs, the greater the volatility
   - Certain compounds and/or formulations are more prone to volatilization (ester more than amine)
   - Can be reduced by incorporation into the soil – adsorption/desorption to soil particles
Herbicide Dissipation

2. Adsorption – binding to soil particles
   - Physical binding through hydrogen bonds is a weak form that results in low binding
   - Chemical binding thru ionic bonds is greater
   - Greater the binding, >persistence, <leaching
   - Higher binding in heavier soils such as clays
   - Greater binding in higher organic matter soils
   - Remember that pesticides are broken down in the soil, or available for crop/weed uptake, when they exist in the soil/water fraction; if they are bound to soil, they generally cannot be degraded.
Herbicide Dissipation

3. Leaching is the downward flow of herbicides in the groundwater
   – effected by soil texture, soil permeability, volume of water flow, adsorption, water solubility of the herbicide
   – May help activity (gets the herbicide into the root zone) but often results in poor weed control (dilution) and potential groundwater contamination

4. Capillary flow is the upward flow of herbicides and salts in the soil/water fraction
Herbicide Dissipation

5. Physical movement of the herbicide can occur through physical movement of soil that the herbicide is adsorbed to.
   - This can occur via wind and water movement
Herbicide Dissipation

6. Breakdown or Transformation

- Photodegradation – this occurs with mainly soil applied materials, UV light breakdown
  - Can be a major form of loss, and results in poor weed control because the herbicide is lost before it can work – occurs with dinitroanaline herbicides
- Chemical – mainly hydrolysis
- Plant detoxification
- Microbial – the most common form of herbicide breakdown in the environment. Microbes use the C in herbicides as a food source.
  - Affected by soil temperature, moisture, aeration, pH, organic matter. Higher temperatures, greater moisture, increased aeration, neutral pH and higher organic matter all result in increased microbial activity and greater herbicide breakdown.
Herbicide Application Methods

1. Pre-plant incorporated (PPI)
   - Applied prior to planting, mixed in the soil
   - Reduces losses from volatility, photodegradation and may be the only way to overcome losses
   - Placement is the key to crop tolerance, the herbicide is placed in such a way that the crop does not take up much while the weeds do. However, incorporating the herbicide too deep can result in crop injury and/or poor weed control.
Herbicide Application Methods

2. Pre-Emergence

- Applied to the soil surface, generally after planting but before crop/weed emergence
- Need rainfall/irrigation for good activity
- Can be used in perennial crops, but need to apply before weed emergence
Herbicide Application Methods

3. At-cracking

- Term that refers to postemergence herbicide applications made to crops as they break, or crack, the soil surface (generally legume/bean crops such as dry beans or peanuts).
- Selectivity is through limited uptake of the herbicide in the terminal bud of the crop, the outer leaves shield the growing point.
Herbicide Application Methods

4. Postemergence

- Over the top of crops and weeds, can be at any time but generally early in the growing season.
- Only applied when needed and can target specific weeds that are present.
- Timing is critical – larger weeds are harder to control.
- Selectivity of the crop and weed is necessary.
Herbicide Application Methods

5. Post-Directed Postemergence
   - Need a height differential between crop and weed
   - Some crops (such as cotton) need a woody stem that limits uptake and therefore damage.
   - Herbicide spray is directed towards the weeds and away from the crop meristem
Herbicide Application Methods

6. Shielded (hooded) Postemergence
   • Non-selective material (generally)
   • Highly dependent on application technology
   • No contact with crop foliage/stem

Hooded sprayer used in cotton. The herbicide is sprayed under the hoods which run between the rows. Generally glyphosate is used.
Herbicide/Plant Interactions

• Factors influencing herbicide movement into plant tissues
  – Polarity (charge or neutral molecule)
  – Formulation
  – Molecular size and weight
  – Adjuvant and carriers (pH, ion content, volume)
Herbicide/Plant Interactions

- Apoplastic movement (thru non-living tissues)
  - Cell walls and xylem flow (water conducting tissues)
  - Move with water flow, diffusion and mass flow
  - Passive process, up to the leaves from the roots, but no downward flow
Herbicide/Plant Interactions

- Symplastic movement (living tissues)
  - Bound by plasmalemma and vacuole membrane
  - Cell interconnected by cytoplasmic strands
  - Phloem movement – source/sink relationship with herbicide tracking and accumulating in regions of active growth
  - Non-uniform movement
Herbicide/Plant Interactions

• Root uptake
  – Primarily apoplastic movement, xylem flow as water, ions, etc. are moved upwards in the plant
  – Herbicides must have the ability to cross the endodermis (Casperian strip), although this is generally not a limiting issue for most
  – Passive movement/diffusion or uptake
Herbicide/Plant Interactions

• Foliar uptake
  – Primarily diffusion into plant cells, then symplastic movement if not a contact herbicide
  – Barriers to foliar uptake
    • Plasmalemma – cell wall, cell membrane, cytoplasm and intercellular membranes
    • Cuticle – thin, waxy coating on the leaf surface; highly lipophillic with numerous polar regions
Herbicide/Plant Interactions

• Foliar uptake
  – Factors influencing uptake from leaf
    • Presence/absence of trichomes, hairs, stomata
    • Leaf age and stage of development (older leaves, less uptake)
    • Leaf angle
    • Environmental – good plant growth, > uptake
    • Light – high light means good growth but also thicker cuticle
    • Temperature and humidity – higher of both causes greater uptake by decreasing drying time and increasing cuticle hydration
Herbicide/Plant Interactions

• Translocation
  – Xylem – passive flow with water column
  – Cell to cell via diffusion
  – Phloem movement via phloem loading
  – Ion trap theory – occurs only with weak acid herbicides. These materials are undissociated in the cell wall due to the low pH (high hydrogen ion content); able to pass through plasmalemma due to lipid solubility; once inside the cell the higher pH causes the compounds to dissociate, cannot pass back out - thus being trapped in the cell (this uses no metabolic energy from the cell)
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