

## Lecture

### Metabolism of Herbicides in Plants

Herbicide selectivity between a weed and crop can be related to differences in:

absorption/uptake, translocation within the plant, and/or metabolism

In the majority of cases selectivity is due to differences in metabolism between the crop and weed i.e. the crop unlike the weed is able to metabolize the herbicide to an inactive form.

#### 1. Definition - metabolism, degradation, molecular modification

metabolism = degradation = molecular modification, all referring to a change in the chemical structure of the herbicide molecule

✓ Any minor change in the herbicide molecule can drastically change the herbicide activity.

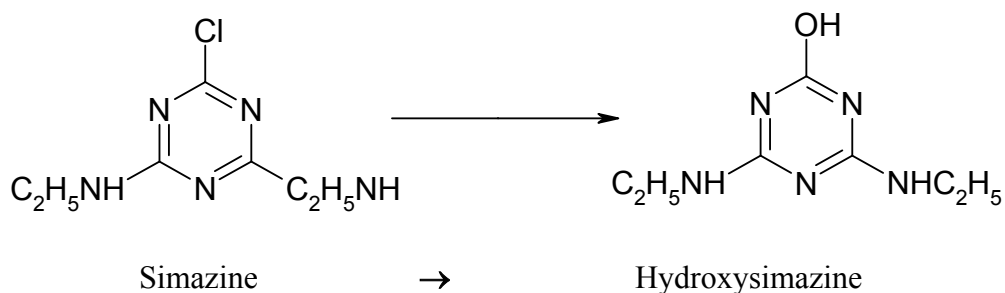
#### 2. Metabolism of a herbicide may result in:

- inactivation of the herbicide - or deactivation where phytotoxicity is reduced; this is the most common result of herbicide metabolism

since plants vary in their ability to modify chemical structures, this determines tolerance

e.g. atrazine is rapidly degraded by corn but not by weeds. Hence the corn is tolerant and the weeds are susceptible. This makes atrazine a selective herbicide

Specific example of herbicide inactivation of Simazine

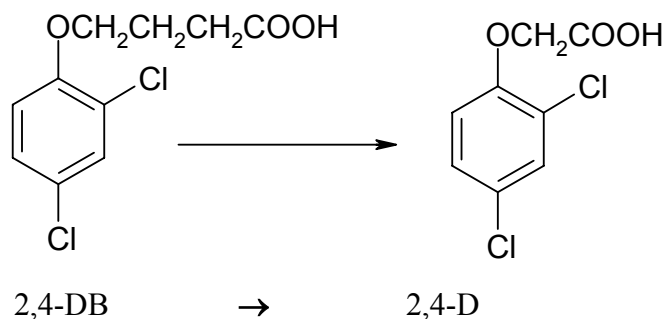


The simazine molecule is dechlorinated (dehalogenation reaction) and the chlorine is replaced with a hydroxyl group. The end product of the inactivation reaction is hydroxysimazine, which is 1000 times less toxic than simazine.

✓ In most cases, crops are able to metabolize the herbicide, but weeds are not.

- activation of the herbicide - in some cases a herbicide is metabolized to a more active form. This is less common than inactivation

Specific example of herbicide activation through conversion of 2,4-DB to 2,4-D



2,4-DB (2,4-dichlorophenoxy butyric acid) is a phenoxy herbicide used in soybeans and alfalfa, which are both legume crops.

$\beta$ -oxidation is a pathway in plants whereby long chain carbon segments are degraded by removing 2 carbons for each cycle of the pathway. By removing 2 carbons from 2,4-DB (butyric acid - 4C's) we are left with the more active form, 2,4-D (acetic acid - 2C's).

The 2,4-D is what kills the weed.

#### ✓ Why are the soybeans and alfalfa not injured?

$\beta$ -oxidation occurs in all plants, but in legume crops the process occurs at a much slower pace. Hence, the susceptible species convert nontoxic 2,4-DB to toxic 2,4-D through  $\beta$ -oxidation, whereas soybeans and alfalfa do not and are therefore not affected.

3. Inactivation of herbicides - herbicide is made less toxic by altering the molecular configuration
  - biochemical reactions - primarily enzymatic reactions that occur within a living plant
  - chemical reactions - breakdown herbicide, but do not necessarily require enzymes
  - conjugation - the herbicide is bound (adsorbed) to another compound, e.g., glucose, amino acids
  - adsorption - herbicide weakly bound to cell wall constituents
4. Specific biochemical or chemical reactions
  - decarboxylation - removal of -COOH group from the herbicide; part of the degradation sequence for many phenoxy, benzoic acid, and substituted urea herbicides

- hydroxylation - the addition of a -OH group to the molecule; often accompanied by removal or shifting of another atom such as chlorine; common among phenoxy, benzoic acid, and triazine herbicides
- hydrolysis - splitting of a molecule through the addition of water; involved in the degradation of carbamate, thiocarbamate, and substituted urea herbicides.
- dealkylation - removal of alkyl side chains from the herbicide; examples include the triazine, substituted urea, carbamate, thiocarbamate, and dinitroaniline herbicides
- deamination - removal of an amine group (NH<sub>2</sub>) from the herbicide
- ring hydroxylation - the addition of a -OH group to the ring structure of the molecule
- dealkyloxylation - removal of an alkyl group with an attached "O"
- beta-oxidation - pathway in plants whereby long chain carbon segments are degraded by removing 2 carbons for each cycle of the pathway
- see Figure 4.18 (Some common reactions involved in herbicide degradation; page 4)

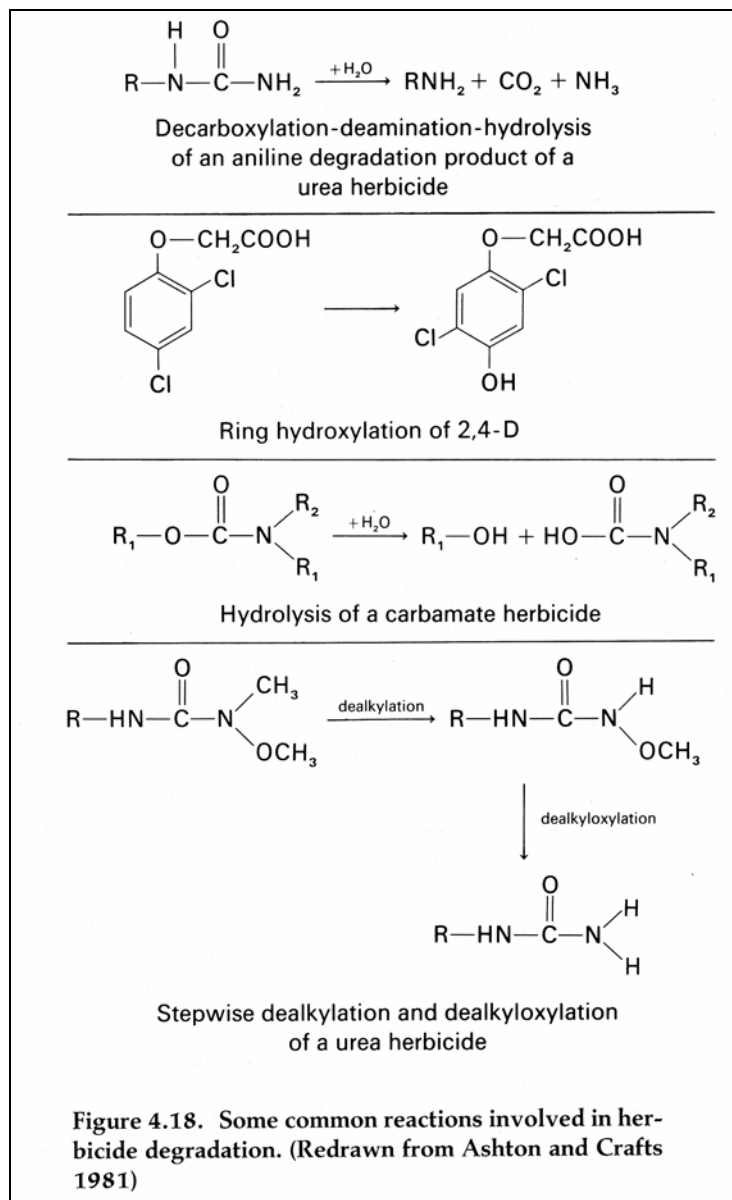
5. Molecular fate of herbicides as described by Shimabukuro (1985) - the metabolism or molecular fate of herbicides was described using a 3-phase process.

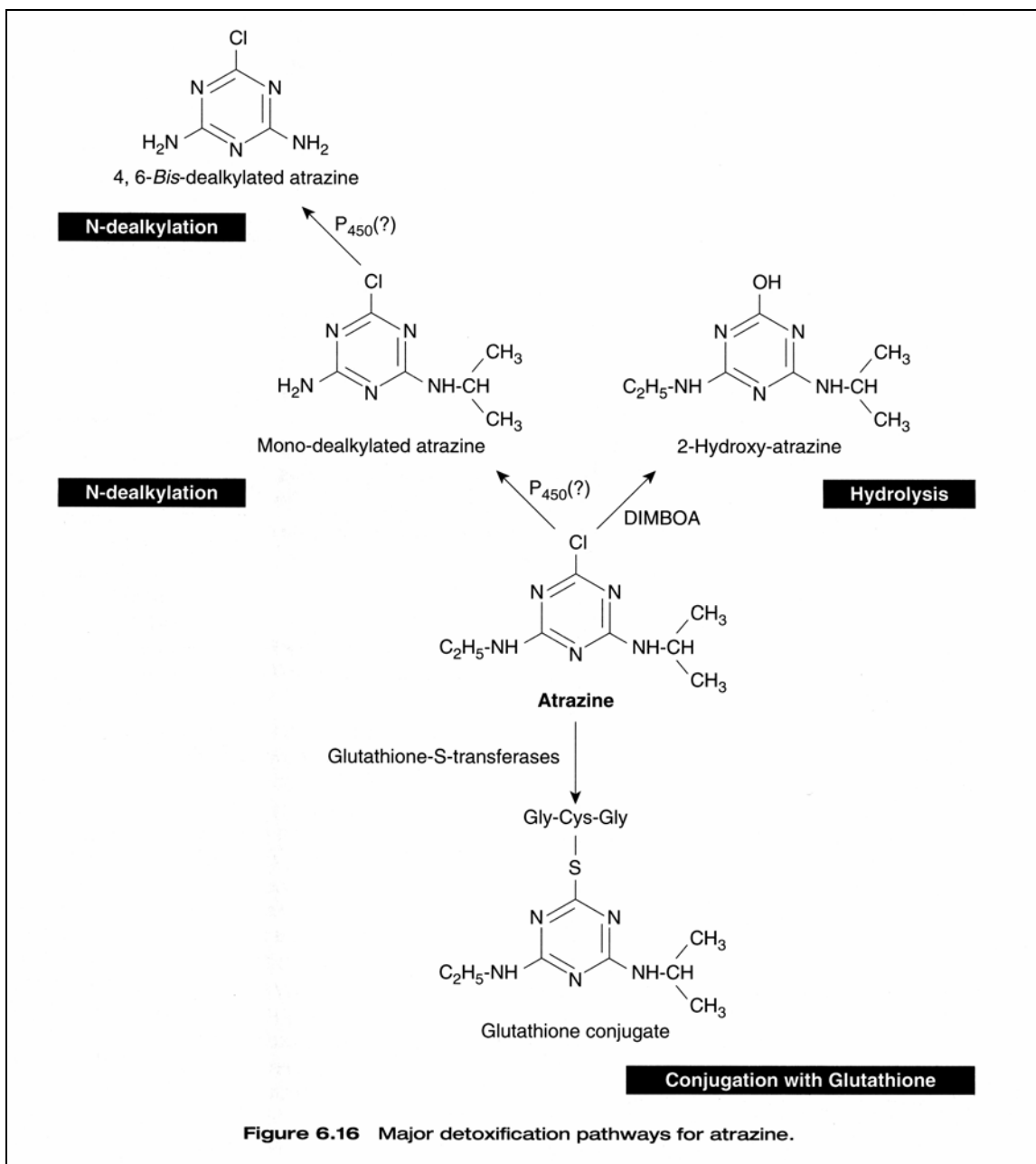
- Phase I reactions - dechlorination, hydroxylation, decarboxylation, dealkylation, oxidation/reduction, and hydrolysis are the initial chemical reactions that occur  
  
These reactions detoxify the herbicide and predispose the resultant metabolites to conjugation.
- Phase II reactions - conjugation with sugars, amino acids or natural plant constituents (metabolites are strongly bound)
- Phase III reactions - these are unique to plants and consist of secondary conjugation reactions or the formation of insoluble bound residues

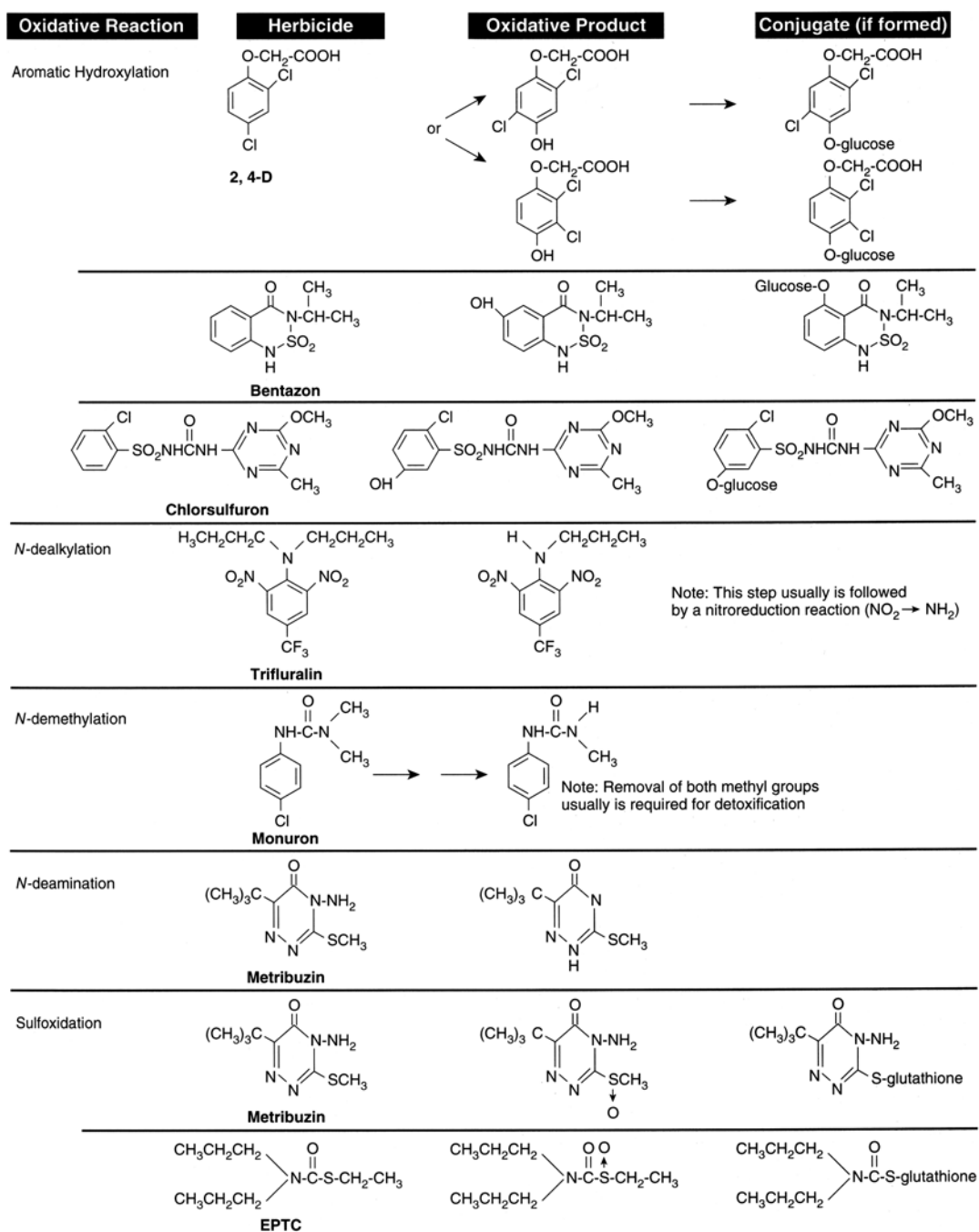
In general, plants "immobilize" these metabolites whereas animals excrete them. In animals, toxins are degraded by the liver and excreted through the kidneys.

Relate my involvement with a student from Environmental Engineering who is working on plants as a "bio-remediation" tool to clean up areas contaminated with toxicants

- see Figure 6.16 (Major detoxification pathways for atrazine; page 5) and 6.14 (Examples of oxidation and conjugate transformations; page 6)







**Figure 6.14** Examples of oxidation and conjugate transformations. These herbicides may be further metabolized, or conjugated or metabolized in other ways, depending on the plant species.