Herbicide Translocation and Metabolism

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Barriers to herbicide absorption

Herbicides are applied to an appropriate site of entry into the plant from where they must move to the appropriate site of action. Sites of entry for soil applied herbicides are young root tissues especially root hairs on dicots (broadleaf) and the crown or coleoptilar nodes on monocots (grasses). The leaves and, to a lesser extent, stems are the sites of entry for above ground herbicide applications. Young root tissues do not have a cuticle so as to not impede water and mineral nutrient absorption. However, mature roots will have suberized tissues that prevent entry (and exit). The first significant barrier to entry for foliar applied herbicides is the cuticle, which is designed for protection and to prevent water loss from the plant. It is comprised primarily of epicuticular wax and cutin with pockets of embedded wax. Nonpolar (oil-like) lipophilic herbicides move more quickly through the waxy portions of the cuticle than the cutin. Polar (water-like) hydrophilic herbicides more quickly through the cutin than waxy portions. Pectin strands and cellulose extending from the cell wall are the next significant barriers for lipophilic herbicides but pose a relatively easy conduit for hydrophilic herbicides. Once past the cuticle, herbicides can move further into the plant along the cell walls and not enter cells through the plasma membrane. Movement outside the plasma membrane is called apoplastic (i.e. the "dead" portion). Movement within the plasma membranes of living cells is called symplastic movement (i.e. "living" portion). Herbicides and other molecules can move from living cell to living cell remaining within the symplasm through plasmadesmata. Entering the symplasm is a significant barrier to herbicide entry, which is determined primarily by the herbicide's partition coefficient, K_{ow}. The K_{ow} of an herbicide is the ratio of herbicide dissolved in octanol to herbicide dissolved in water. A high K_{ow} is indicative of low polarity and relative ease in passing through the plasma membrane (e.g. atrazine, oxyfluorfen, fluazifop-p-butyl). Herbicides such as glyphosate and paraquat have low K_{ow}'s and thus have difficulty with this barrier.

Herbicide Movement inside Plants

There are three processes by which herbicides move inside the plant: diffusion, active transport, and bulk transport. Most herbicides enter plant cells from the apolasm to the symplasm by simple diffusion: a passive process of random movement from high concentration to low. Sometimes protein channels in the plasma membrane provide a path of lesser resistance to herbicides and similar molecules than moving directly through the plasma membrane. Active transport requires an expenditure of ATP to drive a proton pump (e.g. ATP synthase) which ultimately establishes an electrical as well as chemical gradient on one side of a membrane relative to the other. Protein carriers imbedded in the plasma membrane then facilitate transport of molecules including herbicides into the symplasm. A phosphate carrier is probably bringing glyphosate into the cell. An auxin efflux carrier transports the herbicide 2,4-D, whereas glufosinate is probably utilizing an amino acid carrier. Bulk transport is the process responsible for most long distance transport inside plants. This passive process (not counting the ATP expended for sugar loading and unloading) occurs apolastically in the xylem or symplastiaclly in the phloem.

The site of action for contact herbicides is the same as the site of entry because they do not move well within the plant. Systemic herbicides usually must move some distance inside the plant to the appropriate site of action. These herbicides use either the transpiration (water) stream of the xylem or translocation (sugar) in the phloem to travel long distances. All herbicides must eventually get to living cells to achieve herbicidal action. Systemic herbicides move in both the symplasm and apoplasm but preferentially in one. Polar (hydrophilic) herbicides tend to move better in the apoplasm because they move through cell walls easily. Nonpolar (lipophilic) herbicides tend to move better in the symplasm because they move easily through plasma membranes. Some herbicides such as paraquat and trifluralin do not move much at all in either symplasm or apolasm whereas dicamba can move equally well in both. Symplastically (phloem) mobile herbicides are typically applied to the leaves (glyphosate, 2,4-D, sulfonylureas) whereas apoplastically (xylem) mobile herbicides are soil applied (triazines, phenylureas). Bulk transport in the symplasm (phloem) moves from photosynthetic sources primarily mature leaves to growth and storage sinks such as flowers, roots, or young leaves. Directionality of transport is from nearest source to nearest sink. Thus upper source leaves tend to feed upper sinks and vice versa. Top to bottom (i.e. polar) transport is achieved for certain weak acids such as auxin according to the weak acid hypothesis (also called the chemiosmotic model or ion trapping). Essentially, protonated (un-disassociated) weak acids in low pH conditions such as occurs in the cell walls can pass into the symplasm with relative ease compared to the deprotenated

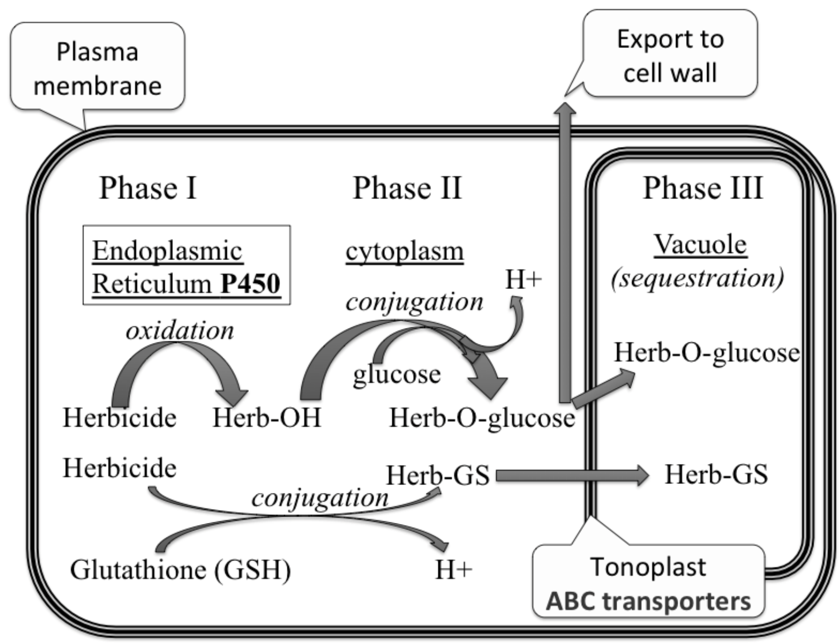

Figure 1. Summary of the three main phases of herbicide metabolism.

weak acid in high pH conditions such as the cytoplasm. An ATP-expending proton pump maintains low pH in the cell walls. Auxin efflux proteins (PIN and PGP) preferentially transport auxins and other weak acids such as 2,4-D from shoot tips toward the roots.

Metabolism

Herbicide metabolism describes the processes by which herbicides are detoxified or activated inside plants. That certain species are better or worse able to metabolize herbicides results in the selective activity of herbicides. Some herbicides such as glyphosate is not readily metabolized inside most plants which explains its broad spectrum activity. Herbicides such as atrazine can be degraded rapidly inside plants where some species are better able than others to detoxify it making it a selective herbicide. Though not common there are several examples of differential herbicide *activation* inside plants that can provide selectivity such as the use of 2,4-DB in legumes where sensitive weeds will beta oxidize 2, 4-DB to form 2,4-D. Differential breakdown is more common and can be divided into three phases summarized in Figure 1.

Phase I

A significant detoxifying mechanism in plants and animals are a family of proteins, which comprise the mixed function oxidases called cytochrome P450 in the endoplasmic reticulum. These enzymes are normally involved in biosynthesis of structural compounds such as lignin but can also oxidize herbicides. Figure 2 summarizes the main oxidation steps performed by these enzymes. Other phase I reactions include reduction by N-deamination (removal of an amino group).

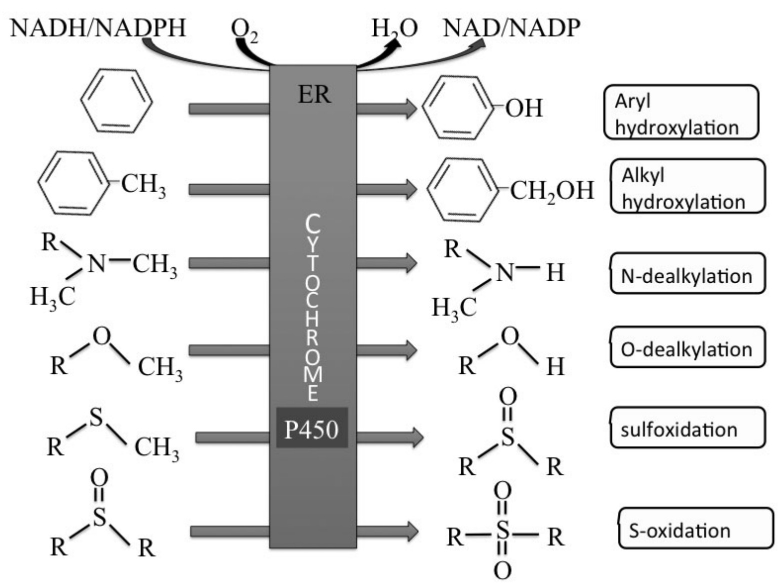

Figure 2. Summary of oxidation reactions that occur in the endoplasmic reticulum by the cytochrome P450 enzymes.

Phase II

Conjugation of oxidized herbicides to sugars, amino acids, glutathione or homoglutathione are examples of phase II reactions in plants. Some plant species can conjugate herbicides without them being oxidized where glutathione or homoglutathione are substrates and glutathione-S-transferase is the enzyme that works on the electrophilic centers of herbicides. Examples of herbicides that are conjugated in this way are the arylophenoxypropionates (-fops), triazines, thiocarbamate (EPTC), and the chloroacetamides (e.g. metolachlor and alachlor). Triazine detoxification occurs readily in plants by one or a combination of three mechanisms: N-dealkylation (minor but may explain cotton and soybean tolerance), DIMBOA-mediated hydrolysis, and glutathione conjugation. Corn possesses all three of the mechanisms, which explains its tolerance of atrazine.

Phase III

Glucosylated herbicides (attached glucose) and glutathione-herbicide conjugates are moved to the extracellular matrix or transported to the vacuole for further processing or storage. The ATP binding cassette (ABC) transporters are responsible for conjugated herbicide transport. Often the final processing step is the attachment of a malonyl group to the conjugate before final transport outside the cell or into the vacuole.

Safeners

The idea to use chemical safeners as "antidotes" to herbicides was developed by Otto Hofman in the 1940's. Most often safeners enhance glutathione conjugation or enhance cytochrome P450 enzymes for plants exposed to these chemicals. Perhaps increased acitivity of ABC transports is another mechanism of safening. Flurazole, dichlomid, benoxacor, and fenclorim are examples of safeners used in grass crops. They may be applied to the crop seed before planting or can be premixed with the primary herbicide. The reduced activity of herbicide mixtures associated with antagonism may be due to a safening effect whereby the herbicides in mixture may be enhancing herbicide metabolism inside plants. Conversely, synergism of herbicide mixtures may be due a decrease in metabolism as occurs in strawberries where teracil damage increases in the presence of fluazifop-p-butyl.

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