Barriers to Foliar Penetration and Uptake of Herbicides

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To be effective, herbicides must enter the plant. This process can occur very quickly or very slowly, depending on the herbicide, formulation, plant, and environmental conditions. For foliar applied (postemergence) herbicides, penetration and uptake can occur through cracks in the leaf surface, stomatal cavities, or by diffusion through the cuticle. Other surface features of the leaf such as trichomes (hairs and glands) can greatly influence herbicide uptake.

Trichomes

Plant leaves can have a variety of trichomes, including glands and simple and/or complex hairs (5). Trichomes on the leaf surface can reduce herbicide efficacy by intercepting spray droplets before they contact the epidermal surface (5). Complex branched trichomes can greatly reduce the number of spray droplets reaching the leaf surface, and even a low density of simple trichomes can reduce herbicide contact with the cuticle. The addition of a surfactant to the spray solutions allows drops to break into smaller droplets when they hit trichomes. This increases the amount of spray solution contacting the epidermal surface.

Cracks in leaf surface

Breaks in the cuticle layer caused by wind, rain, insects and other agents can increase the absorption of herbicides, particularly water soluble compounds. In some mature plants, such as English ivy, intentionally injuring the foliage and stems with a metal rake can create avenues for significant herbicide uptake. Under normal conditions, however, cracks and tears in the foliage are not major routes of herbicide entry.

Stomatal entry

Most weeds have stomata on both the upper and lower leaf surfaces (5). Although volatile herbicides easily penetrate stomata, stomatal penetration by an aqueous solution is not possible unless the surface tension of the spray solution is significantly reduced. Most surfactants are incapable of reducing surface tension enough to allow stomatal penetration. Prior to the development of the organosilicone surfactants, stomatal infiltration of herbicides into the leaf was considered to be of minor importance. In contrast to other wetting agents, the organosilicone surfactants can reduce surface tension to levels low enough to allow stomatal infiltration of aqueous spray solutions (10, 11, 12). When stomatal penetration occurs, it is greatest in the morning when stomates are more likely to be open.

Cuticle

The cuticle is a thin layer (0.1 to 10 μM thick) on the outer wall of leaf epidermal cells. Cuticles can also cover specialized structures like trichomes, pore walls of stomata, and guard and epidermal cells lining the substomatal chamber (3). The primary function of the cuticle is to protect and prevent uncontrolled water and gas loss from plant tissues leaf surfaces. The cuticle typically acts as the primary barrier to foliar applied herbicide penetration into leaf tissues. However, for foliar herbicides to be active they must be able to penetrate the cuticle and subsequently enter the cell.

The cuticle differs in structure and composition within and among species (3). As a result, herbicide permeability across the cuticle also differs greatly among plant species and stages of leaf development (9). For example, among ten plant species tested, the range of 2,4-D permeability across leaf cuticles differed by over 200-fold (7). Any environmental condition that directly effects the cuticle will have some effect on herbicide absorption.

The cuticle is composed of three distinct substances; waxes (epicuticular and embedded), cutin, and pectin.

<u>Waxes</u>

Waxes are very lipophilic and non-polar. They effectively prevent water from penetrating into the underlying cells. Cuticular waxes are composed of two types, epicuticular and embedded. The epicuticular wax is the most significant barrier to the penetration of water-soluble herbicides. In contrast, lipophilic oil soluble or ester herbicide formulations easily penetrate this waxy layer by simple diffusion. In general, epicuticular wax comprises only about 10% of the total mass of the cuticle (9).

Epicuticular wax

Epicuticular wax consists of a variety of long chain even numbered (C_{22}-C_{24}) primary alcohols, acetates, aldehydes, and fatty acids, and their hydroxy- and oxyderivatives, as well as odd-carbon-numbered (C_{17}-C_{35}) hydrocarbons, secondary alcohols, ketones, ketols, and β-diketols (3). Surface wax deposits can vary among species and these differences influence herbicide wettability and penetration into the foliage (5).

The very hydrophobic epicuticular wax can lack surface features (amorphous), or can be semicrystalline or crystalline in nature (5). The surface-fine structure of the epicuticular wax can be characteristic of a species (3, 4). Crystalline wax domains reduce retention of the spray solution on the cuticle surface compared to a smooth surface (6). Even surface wax roughness can greatly influence herbicide penetration (1). Since epicuticular crystalline wax domains are often inaccessible to solutes, they can slow herbicide penetration into the leaf tissue (8). Differences in epicuticular surface features can exist among plants of a species or on leaves of an individual plant. Leaves of different ages or from plants grown under various environmental conditions can have different surface wax patterns that influence the rate of herbicide uptake (9).

Surfactants are well known to increase the portion of the leaf surface covered by water-based spray solutions (5). Even in the presence of a surfactant, herbicides in aqueous solutions rarely spread out evenly over the leaf surface following foliar application (5). In fact, they tend to accumulate in the depressions above anticlinal walls (perpendicular to leaf surface) after individual spray drops dry on the leaf surface. Leaves with little epicuticular wax have spray deposits that spread out over larger areas of the surface. In contrast, leaf surfaces with greater epicuticular wax development have deposits that cover a lower proportion of the leaf. Since less herbicide is in contact with the leaf surface, absorption is generally reduced (5).

Foliar applied herbicides formulated as suspensions, such as wettable powders or flowables, have only a fraction of the particle surface in direct contact with the cuticular surface (5). This limits the absorption potential of the active ingredient. The addition of a surfactant or crop oil concentrate to the tank mix can increase absorption, provided the herbicide is soluble in the adjuvant. Many foliar applied suspensions accumulate high concentrations of herbicide around the margin of the dried droplet. The margins of these ring-like deposits have stacked layers of particles. This leads to reduced leaf contact and decreased rates of absorption (5).

Emulsifiable concentrate formulations can appear as discrete droplets on the leaf surface or can form crystallize deposits. Differences in the type of spray deposit on the leaf can influence herbicide absorption and performance. Herbicide absorption is usually greatest in emulsifiable concentrate formulations that do not crystallize on the leaf surface (5).

Embedded waxes

In addition to deposits of epicuticular wax on the leaf surface, most cuticles also have a layer of wax oriented perpendicular to the cuticle surface embedded within the cutin matrix (2, 3). These waxes can also provide a pathway for non-polar herbicides absorption. Polar (hydrophilic) herbicides are not required to transport through these waxes as they can more readily move through the adjacent cutin layer.

Cutin

The majority of the cuticle volume consists of cutin. Cutin is thought to primarily function in protection of cellular constituents by absorbing UV radiation. Cutin is hydrophilic, polar with a negative charge and is composed of highly cross-linked polymers of hydroxylated fatty acids (3). Cutin is lipophilic and will hydrate in the presence of water. The water imparts a hydrophilic component to the cuticle for diffusion of water-soluble herbicides. Because of the presence of embedded waxes within the cutin, lipophilic (non-polar) herbicides can also readily move through this layer once they have diffused across the epicuticular wax. Thus, the cutin is not considered a major barrier to lipophilic or particularly hydrophilic herbicide movement.

Pectin

Pectin strands are composed of polymers of galacturonic acid and are located at the cutin/cell wall interface or dispersed within the cutin layer. They are very hydrophilic and, like cutin, provide pathways for water-soluble herbicides when hydrated.

Herbicide penetration through the cuticle

The ability of a foliar applied herbicide to be absorbed through the epicuticular wax of the cuticle depends upon two factors; the partitioning of a chemical into the waxy layer (partition coefficient) and its mobility within the epicuticular wax (diffusion coefficient) (6, 9). Non-polar (lipophilic) herbicides, such as ester formulations, are highly permeable and mobile in waxes. These compounds can easily penetrate the epicuticular wax and move through the embedded wax. Most herbicides, however, are polar and are applied in an aqueous form. Poor performance of water-soluble herbicides is often attributed to limited penetration across the epicuticular wax layer (2, 9). The absorption of these herbicides could be improved through increased partitioning of the active ingredient into the cuticle, or enhanced mobility of active ingredient within the cuticle. Surfactants accelerate the rate of herbicide uptake by expanding the contact area on the leaf surface and by increasing the permeance of herbicides in the cuticle (6). The permeability of herbicides across cuticles differs among plant species and can be greatly influenced by environmental conditions, as well as adjuvants (9).

Herbicide movement through the cuticle is a diffusion-controlled process (2, 9). Lipophilic herbicides diffuse across the non-polar waxes much faster than water-soluble compounds. Surfactants are typically added to formulations containing water-soluble herbicides to maximize leaf coverage of the spray solution and to increase the diffusion coefficient of the herbicide. This will be discussed in greater detail in the next presentation.

For optimum herbicide penetration, there must be a balance between herbicide concentration and coverage on the leaf surface. Higher herbicide concentration in a low volume spray solution increases the driving force for diffusion. However, poor coverage reduces the surface area where penetration can occur. By comparison, very low surface tension of a high volume application can maximize the surface area covered, but may reduce the driving force for diffusion by lowering the herbicide concentration in the spray solution.

Cell walls

Once a herbicide has penetrated the cuticle it encounters the cell wall. Cell walls provide mechanical stability and protection to the plant cell. They primarily consist of cellulose, which is very porous. Although both polar and non-polar molecules can easily move through the cellulose, compounds with >700 mw (molecular weight) do not easily diffuse through the cell wall due to their size. For this reason, no commercially available herbicides have a molecular weight greater than 700.

Herbicide uptake across membranes

The final barrier for entry of herbicides into the cell is the plasma membrane (cell membrane). Cell membranes regulate the internal chemical environment of the cytoplasm. Herbicide movement across the plasma membrane can be through two processes, non-facilitated diffusion and carrier-mediated uptake.

Nonfacilitated Diffusion

Most herbicides move across the plasma membrane of plants by non-facilitated diffusion. This process is often called simple diffusion. Those that diffuse across the membrane can be divided into two groups based on their physiochemical characteristics. These include lipophilic neutral (lacking charge) molecules and lipophilic molecules with a functional group sensitive to pH. This latter group (weak acids) can dissociate into a less lipophilic ion.

Lipophilic Neutral Molecules

Lipophilic, neutral herbicide molecules are thought to passively diffuse very rapidly across the lipid bilayer of plant membranes down their concentration gradient. The plasma membrane is not a barrier to their absorption, and uptake of these compounds is independent of pH. Many herbicides, including the triazine compounds, penetrate plant cell membranes by simple diffusion.

Lipophilic Molecules with Functional Group Sensitive to pH

Lipophilic herbicides with a functional group sensitive to pH are referred to as weak acids. They typically have pK_a values between 2 and 5. At the pK_a value weak acid herbicides exist at a 1:1 ratio in both the neutral undissociated form and as the anion. The undissociated acid freely diffuses across the plasma membrane because cell membranes are more permeable to undissociated, neutral molecules compared to dissociated, charged molecules. Once in the alkaline compartments of the cell (cytoplasm), the neutral acid form releases the hydrogen ion (acid group) and the herbicide becomes negatively charged. This disassociation process creates a concentration gradient for further influx of the neutral acid form. This process results in accumulation of the anionic herbicide in the cytoplasm. The negatively charged molecule in the cytoplasm has a low permeability across the plasma membrane and cannot readily move out of the cell. Thus, weak acid herbicides accumulate in the cytoplasm by an ion trapping mechanism. These compounds nearly always translocate in the phloem via the symplastic pathway.

Carrier-Mediated Uptake

Some herbicides are moved across the plant membrane very slowly. A protein transport carrier may limit the rate of uptake. Evidence suggests that uptake of 2,4-D (also a weak acid), glyphosate, glufosinate, and paraquat is via a carrier-mediated system. The carrier in these cases is a protein that typically transports other cellular constituents. Once these herbicides have entered the cell they do not move back into the apoplast (cell wall) to any degree. Like the weak acid herbicides, they are translocated primarily within the symplastic pathway.

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