Characteristics of Herbicide Distribution as Patterns for Nematicide Behavior[1]

D. E. BAYER[2]

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In current agricultural practices the foliar application of pesticides for the control of unwanted pests plays a major role in economic crop production. The penetration of foliar-applied pesticides is strongly influenced by the plant surface, the spray solution, and the environmental conditions before, during, and following application. The biological activity of a herbicide has been shown to be influenced by the physico-chemical properties as well as the rate and manner in which it was applied to the leaf (11). The interactions between the plant and the pesticide will govern the quantity that will enter the plant. The question of why some pesticides are translocated within the plant, and others are not, is of considerable importance and could be used to predict the systemic properties of pesticides. Many pesticides are incapable of being transported in the symplast from external applications because the physico-chemical properties, such as polarity, inability to move across membranes, adsorption to various cellular components, etc., prevent their entry into the symplasm. If they do enter, their movement is prevented.

Translocation of assimilates (photosynthates) in plants involves both a metabolically active source (area of synthesis or high concentration) and a metabolically active sink (area of utilization or storage). Thus, assimilates will move through the sieve elements in the direction of the sink and at a rate determined by the sink strength. A unique feature of the phloem is the ability of the materials in the phloem to move out of the sieve elements or into the sieve elements at any point along the system.

This report will present some of the current ideas or hypotheses currently being developed regarding the use of foliar applied herbicides with data to illustrate the significance of the major concepts that may be applicable to nematicides.

LEAF SURFACES

The topography of the leaf surface has been shown to be closely correlated with the type and amount of waxes present (2,6). This waxy layer on the outer surface of the leaf is generally the first barrier through which a foliar-applied pesticide must pass. The morphology of the surface waxes is extremely variable, and the extent to which the surface waxes impede penetration is unclear. However, they do influence the overall process by interfering with interception and retention of the spray droplet by the leaf. Of primary importance is the need to obtain intimate contact between the spray droplet and the surface of the leaf. The liquid-solid interactions that occur on the leaf surface depend on the pesticide (formulation) and the leaf surface. Sargent (8) has suggested that there are three properties at the leaf surface that will affect this interaction: the degree of surface topography, the presence or absence of a film of air between the pesticide droplet and the leaf surface, and the nature of the chemical groups associated with the wax or cutin on the surface of the leaf.

The size and shape of the epidermal cells, including anticlinal cell wall depressions, position of stomates, and guard cells, as well as the presence or absence of trichomes, have a strong influence on the degree of droplet spreading and ultimate penetration of the applied herbicide.

The role of the stomate in uptake of foliar-applied materials is still under discussion. However, it has been shown that significant uptake of herbicides does occur through astomatous tissue (1,6). Stomatal uptake is enhanced when leaf morphology and surface energies allow the spray solution to drain into depressions and stomatal chambers. In the leaf epidermal layer, the guard cells and the regions over the anticlinal walls appear to be the preferred

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[2] Professor, Department of Botany, University of California, Davis, CA 95616.

sites of absorption. The fact that the herbicide tends to accumulate in the depressions overlying the anticlinal walls might in part explain this phenomenon. When a herbicide is applied at 748 or 374 liters/ha, it tends to accumulate over the anticlinal walls leaving a honeycomb appearance on the leaf surface. At 117 liters/ha or less, the herbicide is randomly deposited in small deposits on the leaf surface indicating that the herbicide is covering both the anticlinal and periclinal walls. The smaller deposits may be a result of decreased droplet size of the spray solution as a result of decreased nozzle orifice used in application. Even on very waxy leaf surfaces these small droplets have been shown to adhere to the surface of the leaf, thus allowing a greater amount of herbicide to be retained on the leaf (4).

The absorption of a foliar-applied material can be considered in terms of three criteria: the quantity of active ingredient deposited on the target surface, the extent to which the target surface is covered, and the presence of the active ingredient in a form readily absorbed by the target surface. Retention of the spray droplets on the target surface depends on the number of droplets lost by reflection and/or runoff after aggregation. The runoff is especially important when high volumes are applied.

The frequency and morphology of trichomes on the leaf surface presents a problem to foliar-applied materials because the trichomes do not function efficiently as routes of uptake. Spray volume, droplet size, and surface tension of the spray solution will all influence herbicide performance. High volumes of spray solution are often used in an attempt to thoroughly wet the surface (4). Large spray droplets tend to shatter when they impinge on a stellate hair, allowing the small droplets to penetrate deeper to the cuticle surface. Small spray droplets tend to be reflected off the hair back into the atmosphere or may just remain lodged on the hair; thus efficiency of absorption is much reduced.

The cuticle refers to the outermost layers of the epidermal cells. It is most generally thought to be composed of wax, cutin, and pectin (2). Each layer should not be considered as discrete and separate but rather as a gradual transition into each of the other layers. Even cellulose is occasionally found impregnating the cuticle. Both the wax and cutin layers are considered to be lipophylic in nature, while the pectin and cellulose are more hydrophylic. The degree of ramification of the cutin layer with pectin varies significantly between species. In some species, such as Indian rubber plant (*Ficus elastica* Roxb.), the pectin layer is quite discrete, while in others it is very diffuse, ramifying the entire cutin layer. Even though the cutin is a highly polymerized layer and considered to be lipophilic in nature (2,6), the embedded waxes or waxes dispersed in the cutin are considered to be the major limiting component of the cuticular layer to the uptake of foliar applied materials.

Differences in foliar absorption of a single herbicide has been shown to be directly correlated with the formulation (Table 1). The more lipophilic formulations, such as the ester formulations, will wet the leaf surfaces better and penetrate the plant cuticle more readily than will the more hydrophilic salt formulations (5). It should be recognized that pesticides are formulated to benefit handling and to enhance biological activity. Often the type of formulation is dictated by the chemical properties of the pesticide. Perhaps there is no readily available solvent system for the pesticide, so the manufacturer may resort to a wettable powder. Or perhaps the dry formulation presents a handling problem, so a flowable formulation is prepared. It should always be remembered that for absorption to take place, the active ingredient must be in a form that can be absorbed by the plant. This effect on efficacy may be seen in Table 2, where propanil was formulated as five different emulsifiable concentrates and sprayed on barnyardgrass [*Echinochloa crus-galli* (L.) Beauv.]. Upon drying, three

Table 1. Influence of different types of formulations on efficacy of 2,4-D applied at 0.6 kg/ha for the control of mustard.

Formulation	Percent controlled
High volatile ester	100
Low volatile ester	96
Oil-soluble amine	89
Water-soluble amine	63
Metallic salt	54

Table 2. Influence of five emulsifiable concentrate formulations* on efficacy of propanil applied at 4.5 kg/ha for control of barnyardgrass in rice.

Formulation	Percent controlled
#1	56
#2	61
#3	47
#4	81
#5	93

*The formulations are identical to those used in Table 3.

of the formulations formed crystals on the surface of the leaf and were no longer in a form that could be readily absorbed by the barnyardgrass. The other two remained in a form that was readily absorbed, and the barnyardgrass plants were killed.

Another aspect emphasizing the need for proper formulation is the need to keep the active ingredient on the target plant. In a laboratory study, the same five formulations of propanil were applied to rice plants which were then placed in a chamber. Air at 10 mph was passed over the foliage and filtered, and the amount of propanil trapped was determined (Table 3). Those formulations that formed loose crystals on the surface of the plants not only provided poorer control of the barnyardgrass plants, but the crystals were free to be dislodged by leaf movement or the wind and fall to the soil or be blown to nontarget areas.

ABSORPTION OF FOLIAR APPLIED HERBICIDES

Those chemicals translocated within the plant to an area where they exert their phytotoxic effect are considered to be systemic, and those that are retained and exert their effect in the underlying tissue are termed contact chemicals. All herbicides must move into the underlying plant tissue before translocation from the point of application can occur or, in the case of contact herbicides, before a phytotoxic response can be accomplished. This movement constitutes the absorption process. This process involves the movement of the penetrating molecules through the wax, cutin, pectin, and cell wall layers (cuticle plus the cell wall) to the plasma membrane. For herbicides whose primary mode of action is the disruption of membranes, the absorption process may be considered to be complete. However, for most herbicides the absorption process also entails the movement across the plasmalemma.

Table 3. Influence of formu'ation* on the amount of propanil dislodged from rice leaves by air moving at 10 mph following a 4.5-kg/ha application.

Formulation	Propanil dislodged (μg)
#1	2.4
#2	1.9
#3	3.3
#4	1.0
#5	.3

*The formulations are identical to those used in Table 2.

Little is known about the movement of pesticides across the plasmalemma. Many studies have suggested that passive movement, as well as a metabolic component of uptake, is involved in the movement of organic compounds across the plasmalemma.

To study the absorption process independently of transport, a somewhat idealized method was developed (9). Thin sections of leaf tissue (4–8 cells wide) were floated in a buffered treatment solution containing radioactive herbicide. Depending on treatment time, the sections were removed from the solution, rinsed briefly, and radioactivity determined, or the leaf sections were desorbed in an equivalent solution containing nonradioactive solution. In this manner, the various fractions (total, exchangeable, and nonexchangeable) were determined. The "total" fraction represented the total amount of herbicide taken up by the leaf sections. The "exchangeable" fraction represented the amount of herbicide that could be removed by washing for 1 hour. The "nonexchangeable" fraction represented the amount of herbicide that remained in the leaf sections following the 1-hour wash period .

Certain herbicides, such as 2,4-D, tend to be accumulated to very high concentrations in the metabolically active tissue, while other herbicides, such as diuron, do not accumulate to high concentrations in the symplast. Herbicides like 2,4-D may accumulate in the symplast to a concentration when egress is more rapid than influx. During this period net concentration will decrease in the cell. At some lesser concentration, influx will again exceed egress and the concentration within the cell will increase. Other herbicides, such as picloram, do not appear to show a major phase of net loss from the tissue.

Temperature has a strong influence on both the absorption and translocation processes. For those herbicides that tend to accumulate in the symplast, absorption increases as temperature increases within the limits of biological activity. However, when translocation is considered, the curve is modified by the physiology of the plant. When temperature approaches approximately 35 C, the absorption process is rapid. However, transport in some plants may be slowing due to physiological reasons, so the concentration of the herbicide in those cells directly functioning in the uptake process accumulate phytotoxic levels of herbicide and are killed. Movement out of those areas is stopped or much reduced. This may be observed as a necrotic spot or contact type burn on the plant.

The absorption process of these same herbicides is also affected by internal moisture status of the plant during the time when influx is occurring. When the internal water stress of field bindweed (*Convolvulus arvensis* L.) is increased from –9 bars to –12 bars, the influx to 2,4-D is reduced over 50 percent (Table 4). There are conflicting reports in the literature whether the absorption process is reduced because of plant water stress, thus limiting translocation, or whether translocation is affected directly. When controlled experiments were conducted to minimize the impact of translocation on absorption, it appeared that internal plant moisture stress directly affected the absorption process of 2,4-D. This does not mean, however, that internal plant moisture stress would not influence the translocation process.

Table 4. Influx of ^{14}C-2,4-D into foliage of field bindweed under various internal moisture stress.

Moisture stress (bars)	Uptake (percent reduction)
0 (Nonstressed)	0
–6	5
–9	20
–12	43
–15	51
–18	57

TRANSPORT OF FOLIAR APPLIED HERBICIDES

Once a herbicide has penetrated into the plant, two predominant types of transport have been reported (3). Herbicides may be grouped into four general categories depending on their translocation characteristics: herbicides that are translocated primarily in the apoplast, herbicides that are translocated primarily in the symplast, herbicides that are translocated in both the symplast and the apoplast, and herbicides that have restricted or no movement in either the symplast or apoplast. Those herbicides that enter via the apoplast, for the most part, are transported and/or remain in the apoplast. Those that enter the symplast remain in the symplast. In addition to these two major classifications are herbicides that exhibit all combinations or degrees between these two extremes. Transpiration is the major driving force for those herbicides that move in the apoplast. The major routes of movement are in the cell walls and xylem stream. These herbicides tend to accumulate in areas where high transpiration or water loss occurs, such as the older, fully developed transpiring leaves and, to a much lesser extent, the stems and younger developing leaves.

Herbicides that move primarily in the apoplast are characteristically applied to the soil where they are taken up by the roots of the plant and moved upward in the xylem stream to be accumulated in the foliage. If applied to the foliage, coverage must be complete to achieve uniform distribution within the plant, because the major direction of movement is with the water to the older, mature foliage where the herbicide will remain until metabolized or lost in some other manner.

Those herbicides that enter the symplast and are translocated in the phloem have been shown to move with the assimilate (photosynthate) stream from areas of synthesis (high concentration) to areas of utilization (low concentration) or storage. Thus, assimilates move "en masse" through the sieve elements in the direction and at a rate as determined by the gradient created by the sum total of the osmotically active solutes. It is important to remember in discussing the fate of herbicide movement in the phloem that the phloem is a distribution system for assimilates serving the entire plant. A unique feature of this system is the ability of materials to move into or out of the sieve elements from adjoining cells.

Translocation of these herbicides is similar to the translocation of naturally occurring assimilates except when the phytotoxic effects induced by the herbicide prevents such movement (3). In a very young seedling, the percentage of actively metabolizing cells would be high, thus a symplastic mobile herbicide would be translocated throughout the entire plant and would accumulate in the areas of high metabolic activity which would include the root tips and apices. As the plant increased in size, the potential for dilution in the plant would become greater and accumulation would become more localized. As the plant flowered and set seed, movement would be to the flowers and seeds; as the seeds matured, transport would diminish and the plant would die.

Carbohydrate reserves in perennial plants are depleted during the early phase of growth and development and are replenished later as the foliage of the plant develops (Table 5). The overall major direction of assimilate movement during the early growth and developmental phase is from the stored reserves to the young developing foliage. If an application of a foliar-applied, symplastically mobile herbicide was made at this early stage of growth, the herbicide would remain in the foliage because the stored food reserves are being utilized for growth and movement is away from these areas and towards the foliage. If an application of the same herbicide was made later in the growth cycle of the plant when assimilates are being translocated from the foliage to the areas of storage, such as full bloom or mature seed stage, the herbicide would be moved along with the assimilates and would accumulate in the developing seed or storage areas.

Table 5. Monthly variation of total carbohydrates in rhizome tissue of undisturbed Johnsongrass, Davis, California.

Month	Carbohydrates (mg/g dry weight)
January	615
February	603
March	610
April*	540
May	500
June	475
July	405
August†	484
September	591
October	602
November	598
December	601

*New growth was being initiated.
†Full seedhead formation, seed maturing.

Those herbicides that translocate readily in both the symplast and the apoplast need to be considered by relating the characteristics of both types. All herbicides, if taken up by the plant, have the potential to be translocated in either the apoplast or symplast, or both. However, many are capable of only limited movement because of physico-chemical factors, including structural requirements. It should be remembered that these classifications (Table 6) are only relative. When a herbicide is listed

Table 6. Translocation patterns of some common herbicides.

Herbicide	Translocation*	
	Symplast (phloem)	Apoplast (xylem)
Amitrole	++	+++
Atrazine	0	+++
Dalapon	++	+
Dicamba	+++	+
Diuron	0	+++
2,4-D	++	0
2,4-DB	0	0
EPTC	0	>+
Fenac	+	++
Glyphosate	++	++
Picloram	+++	++
Simazine	0	+++
2,4,5-T	++	0
2,3,6-TBA	++	+++

*0 = restricted to no evidence of movement; + = limited translocation; ++ = intermediate translocation; +++ = translocated readily.

as being mobile only in the apoplast, it actually moves into the symplast and is swept along in this system; however, it has such a high affinity for the apoplast it is rapidly partitioned out of the symplast and back into the apoplast. The reverse is true for those indicated as moving only in the symplast. For those herbicides that move in both systems, the degree of affinity for the apoplast or symplast, or the ability to move into or out of one system and into or out of the other, will determine which system it moves in and to what extent (10).

Those herbicides that exhibit limited movement in plant tissue are usually restricted because of structural requirements, solubility, adsorption, etc. These herbicides must be applied in such a manner that limited movement will allow them to reach their site of herbicidal action.

There is a group of herbicides that will translocate in the symplast, accumulate in the roots (especially root tips), and leak out of the roots to the surrounding environment (7). They then may be tied up in the surrounding environment or they may be resorbed by the roots. This phenomenon has been known for some time but has become of interest recently with exudation of such organic substances as herbicides that were applied to the foliage. The most prominent classes or families of herbicides that leak out of roots following a foliar application are benzoic acids, picolinic acid, phenoxyacetic acids, and phenylacetic acids. The quantities that are exuded from roots range from less than 1% to over 10% of the amount applied to the foliage (Table 7). Exudation appears to be dependent on the rate applied, the presence of binding to plant and constituents, and the rate of metabolism of the compound by the plant. In general, those herbicides that are not translocated readily or are easily metabolized are not exuded from the roots.

The chemical structure of the molecule is a critical factor in determining whether a herbicide will be exuded from plant roots. Such factors as number of substitutions, position, nature, etc., are all critical components of the molecule. The area or zone of the root most actively involved in the exudation process is the zone of root elongation .

Table 7. Amount of herbicide exuded from roots of bean plants from a foliar application of 100 μg herbicide.

Herbicide	Exuded (μg)
2,4-D	2
Dicamba	11
2,3,6-TBA	7
Fenac	8
Picloram	5
Glyphosate	1

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