INSECTICIDE APPLICATION: THE DOSE TRANSFER PROCESS

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In the broadest sense, the application of pesticides involves the transfer of a toxicant from the manufacturer to the target organism. This is the dose transfer process, which can be broken down into several major events. However, difficulties at any step can result in a loss of biological activity, excessive environmental contamination or both.

The dose transfer process is a roadmap for the events that take place in delivering a toxicant to a target organism. In field agriculture, a small quantity of toxicant must be spread over a large area (acres or hectares). On a smaller scale, the same process is used for home garden and turf application. However, many steps in the dose transfer process are reduced when traps are used (e.g., cockroach and ant control in houses), or when the toxicant is used as a barrier (e.g., treated lumber for insect and fungus control). Each step in the dose transfer process is unique for each toxicant, its formulation, its intended use and the environment where it will be used. A general outline of the steps in the dose transfer process and emphasize their interrelatedness is presented here. While most applicable to water-dispersed toxicants applied to field crops via atomization through a small orifice, the discussion could be applied to most pest control activities with some judicious modification (Fig. 1).

The act of formulation is the addition of chemicals other than the toxicant or diluent to the overall sprayed product. These chemicals are collectively called ‘adjuvants.’ The manufacturer of the toxicant, distributors of the toxicant and persons involved in applying the toxicant determine the formulation that is applied to the field. While the applicator is not usually thought of as a formulation chemist, he is altering the physico-chemical properties of the toxicant-diluent mixture when adjuvants are added. Usually the objectives of adding adjuvants are: 1) consumer usability; 2) dispersal in diluent; 3) retention by foliage; 4) reduced redistribution through the drift of small droplets in the air, or the washing off of the toxicant from rainfall; 5) improved biological activity, including improved pick-up of the toxicant by the insects and redistribution to the chemically active site in the insects; and 6) correction of existing problems like the presence of specific ions in the water used for the diluent.

This description of the dose transfer process focuses on the application of toxicants with water as a diluent. The second most common diluent is oil. As oil is different from water, the following discussion may not always apply to applications with oil as the diluent.

Consumer usability

Consumer usability doesn’t fit in the dose transfer process because it is strictly a human use and safety issue. A colorless, odorless toxicant can be made less hazardous by including an odiferous adjuvant (= stenching agent) in the formulation. Other issues include ease of removal from the container, or increase the shelf life of the product. While addressing these issues may result in formulation changes that affect toxicant efficacy, the goal is not related to the manipulation of toxicant functioning. Therefore, consumer usability is not listed as part of the dose transfer process.

Spray tank

Dispersal is first affected by the chemistry of the different formulation components interacting with each other and the diluent. Water is a common diluent for high volume application (100 gallons per acre). Many pesticides are hydrophobic (repel water). Therefore, additional chemicals are needed to keep the toxicant suspended in the diluent. This is done with chemicals that promote the formation of an emulsion (emulsifiers), or that promote the formation of a suspension (anti-flocculating agents). These approaches lead to the formation of two important classes of pesticide formulation: ‘Emulsifiable Concentrates (EC)’ and ‘Suspension Concentrates (SC).’

Following the addition of chemicals (toxicant(s), formulation components and adjuvants) to the spray tank, the initial goal is to distribute these chemicals uniformly throughout the diluent. This can be achieved through agitation of the carrier liquid and the addition of dispersing agents. However, vigorous agitation is not always a guarantee of proper mixing. Interactions between the types of agitation (e.g., paddle mixing, recirculating pumps) and the shape of the spray tank can leave areas of relative calm where formulation components or toxicants can separate or settle out of solution. Where agitation is provided by recirculation through a centrifugal pump, the heat and friction from the pump may promote chemical reactions that alter the expected behavior of the atomized spray. An example of this would be the addition of long chain polymers for drift control. The mechanical action of the pump breaks the long chains, thereby reducing their effect on the atomization properties of the liquid. Dispersing agents that can be added include emulsifiers (surfactants used to mix oil and water), buffers (solubility is sometimes pH dependent), and anti-flocculants (keeping small particles suspended in water).

Atomization

In some way, the toxicant must be distributed over the target area. While other methods are used (e.g., dusting, painting), a common approach is to atomize a liquid containing the toxicant and distribute the resulting droplets over the target area. This can be done in several ways, among them are: 1) hydraulically forcing fluid through a small orifice (hydraulic sprayers); 2) use a high speed air stream (mist blowers); 3) placing liquid on a rapidly spinning disk or cage (Controlled Droplet Applicators [CDA] like spinning disks and rotary cage atomizers); 4) using a hot and rapidly moving air stream (thermal foggers); 5) electrohydrodynamically. The general process whereby the bulk liquid is broken up into millions of small droplets is similar for all these application strategies.

In hydraulic sprayers, the most common approach to atomization, a liquid is forced through a small orifice under pressure. At pressures close to atmospheric pressure, the liquid flows out of the orifice as a stream because surface tension forces exceed the energy from internal and external sources. Increasing pressure will increase the internal turbulence in fluid flow and increase the velocity of the liquid exiting the orifice relative to the surrounding air. Low-pressure application pressures are 15 to 40 psi. At some point below these pressures, sufficient energy is imparted to the liquid stream to cause it to disintegrate into small droplets, and increasing pressure results in smaller droplet sizes. Most hydraulic atomizers exhibit three modes of liquid sheet disintegration: rim disintegration, perforated sheet disintegration, and wavy-sheet disintegration. Rim disintegration is droplet formation from a thickened rim at the leading edge of the liquid sheet (usually occurring in high viscosity and high surface tension liquids). Perforated sheet disintegration takes place in holes that develop in the sheet. Wavy sheet disintegration takes place due to oscillations that tear off droplets at the leading edge of the sheet. In all three cases, ligaments form and disintegrate to produce droplets. However, droplets produced from rim disintegration tend to be larger. Wavy sheet disintegration produces a highly variable range of droplet sizes. Thus, the relative contribution of the different modes of liquid sheet disintegration will determine the size range of droplets produced and the abundance of droplets of a particular size within this range. Droplet sizes within the spray cloud are determined by the thickness of the liquid sheet from which the droplet originates, with larger droplets being produced by thicker sheets. The droplet size range in the spray cloud is also dependent on the velocity of the sheet relative to the surrounding air, and the liquid properties of the atomized fluid (e.g., viscosity, surface tension). Other processes involving high pressures can also atomize a fluid. However, all of them ultimately rely on the Rayleigh mechanism, so named because Lord Rayleigh postulated the breakup of a liquid stream first by ligament formation, then by ligament disintegration into droplets.

The large droplets produced by primary atomization may undergo further disintegration. In still air, the surface tension of the liquid will create spherical droplets because a sphere minimizes the strain within the droplet. It also minimizes the surface area exposed to the air. However, the velocity of the droplets creates air turbulence, and the process of atomization produces a vacuum that also creates turbulence. Also, the droplet is elongated while attached to the ligament, and relaxation of this deformation following detachment from the ligament produces additional stresses. If these forces exceed the surface tension, the droplet will disintegrate by one of three processes described by the shape of the parent droplet prior to breakup: lenticular deformation, cigar-shaped deformation, or bulgy deformation. The breakup of droplets is termed secondary atomization.

Droplet diameters range in size from under 1 μm (1/1,000 mm) to over 1 mm depending on the process used to form them. For field application of pesticides with a low-pressure (15 to 40 psi) hydraulic nozzle, a typical droplet size range is from 50 to 1,000 μm in diameter. Some high-pressure (2,500 psi) hydraulic sprayers used in greenhouses have a droplet size range of 1 to 300 μm in diameter. These ranges would be typical for water, but small quantities of adjuvants (e.g., surfactants or polymers) can change these ranges significantly. ‘Surfactants’ are surface active agents.

Measurement - The output of atomization devices needs to be measured to maintain proper functioning of the equipment and to develop new methods for improving the pesticide application process. Methods of evaluating the output from nozzles can be categorized as quantitative and qualitative. Quantitative measures are most useful for equipment maintenance. These approaches include measuring the output of individual nozzles with a bucket to check for plugged or damaged nozzles. At a finer resolution, smaller containers, or a sheet of corrugated roofing material could be used to measure the fluid deposited over a specific area. This approach would also detect plugged nozzles, but would also detect proper alignment of the nozzles along the boom. While these measures improve the uniformity of toxicant distribution over a field by aiding in equipment calibration, they are not designed to provide sufficient detail for evaluating coverage of individual plants (or leaves) within that field.

Devices for measuring atomization characteristics of nozzles are categorized as mechanical, electrical and optical. Furthermore, the techniques are grouped as intrusive and non-intrusive. An example of an intrusive mechanical approach would be to use several vials placed in different parts of the spray cloud. One then measures the liquid collected per vial over some time interval, much like what is done for equipment evaluation. This provides some measure of uniformity across the spray cloud for individual nozzles, and can also be used to measure output from several interacting nozzles. However, describing the spray cloud in terms of droplet sizes, numbers and velocities provides a better picture of the output of a specific nozzle. The factors to consider when selecting a technique for measuring spray cloud parameters include the effects of spatial sampling versus temporal sampling (factors like equipment cost are not considered here). Spatial sampling describes the droplets that pass through a specific volume in an instant in time. Methods for spatial sampling include high-speed photography and laser holography. Temporal sampling measures droplet sizes that pass through a specific volume over some time interval. Methods for temporal sampling include collection techniques and optical instruments. One collection technique is droplet freezing by injecting liquid nitrogen into the spray cloud. Balls of ice drop into a collection pan and are subsequently sieved. The mass collected in each sieve is divided by the average diameter between the next largest sieve and the current sieve and the numbers of droplets collected can then be estimated. These types of collection techniques are not usually used for assessing agricultural sprays. Spatial drop size data may be converted to temporal data by multiplying the size-specific droplet velocities by the droplet sizes. Temporal sampling has been suggested as the most appropriate method for agricultural uses. Optical instruments for sampling spray clouds include the Malvern particle sizer and the Phase Doppler Particle Analyzer (PDPA). The Malvern is a nonintrusive technique for measuring droplet sizes. The device is based upon a Fraunhofer diffraction of a laser beam. The PDPA is another nonintrusive approach based on work by Bachalo. However, it measures droplet velocity, and then estimates the numbers and sizes of droplets that passed through the probe volume while it was measuring other droplets. The PDPA uses a beam splitter to create two in-phase beams of coherent light. The point where these beams cross is the area that is measured. Droplet sizes are based on the interference fringe pattern as detected by three successive independent sensors. Droplet size is estimated based on the phase shift of droplets as each sensor detects their fringe pattern.

Characterization - Characterizing the spray cloud is done with descriptive statistics and mathematical models for which parameters are estimated based on measurements. At present, the most common model is the Rosin-Rammler droplet size distribution function that was based upon work done by these authors for describing particle sizes in powders, or a modified version of this model based on work by Rizk and Lefebvre. The advantage of using a model is that droplets that were not measured (for whatever reason) can be included in the calculation of descriptive statistics. However, regardless of the approach used, the data need to be summarized for comparative purposes and to provide concise inputs for studying the effects of atomization on retention and biological effect. Variables include droplet surface area, droplet diameters, droplet volumes and droplet velocities. These variables can then be described using the mean, median, or mode. Additionally, some description of the dispersion of the data around these values is often useful. These measurements can apply to the entire cloud, but typically scans are made along one axis of the spray cloud. For a flat fan nozzle, the z-axis is parallel to the flow out of the orifice with the origin at the center of the orifice; the x-axis is perpendicular to the z-axis and oriented along the major axis if droplet dispersion in the x-y plane forms an ellipse. This can be broken down further by taking point measurements at discrete intervals throughout the x-y plane at one or more points along the z-axis. However, it is not clear how these measures of spray quality can be used to predict toxicant retention on plant surfaces, or ultimately, the biological effects of the application.

Post-atomization - Following atomization, droplets must travel through the atmosphere to arrive at their target. Two forces act to alter droplet sizes arriving at the plant surface: evaporation and friction with the atmosphere. Evaporation changes the droplet size, and for any evaporation rate, the change will be greater in smaller droplets than in larger droplets; i.e., the smaller droplets will get smaller more quickly than will the larger droplets. In some cases, the aqueous component may completely evaporate, leaving only non-volatile formulation components. Friction with the atmosphere is important because smaller droplets loose velocity more quickly than larger droplets, and the terminal velocity of smaller droplets is much lower than for larger droplets. Consequently, small droplets do not travel as far nor penetrate as deeply into the crop canopy. However, small droplets can be entrained in the air turbulence formed by the wake of a passing larger droplet (Table 1).

Terminal velocities of droplets of water falling through still air.

Droplet diameter (µm)	Droplet volume (µl)	Terminal velocity (m/s) [mph]	Extinction time (sec)[1]	Time to fall 18" (0.46 m) in sec
10	5.24 x 10^{-7}	0.003 [0.007]	0.568	152.4
50	6.54 x 10^{-5}	0.072 [0.161]	14.205	6.4
100	0.00052	0.253 [0.566]	56.818	1.8
500	0.06545	2.051 [4.588]	1420.455	0.2
1000	0.52360	3.869 [8.655]	5681.818	0.1

1: Extinction time is estimated based on 20°C ambient temperature, 80% relative humidity, and a temperature difference of 2.2°C between wet and dry bulb thermometers.

In the application of pesticides, one cause of toxicant loss is the drift of small droplets away from the field. Drift may occur when the wind speed "up" (away from the crop canopy) exceeds the terminal velocity of the droplet. Under such conditions, the droplet will not fall onto the crop, and any lateral wind has the potential to move the droplet outside the field boundaries. Given sufficient wind, even the largest droplets will become susceptible to drift. While drift is a loss of toxicant out of the field, some wind-generated turbulence can aid deposition by moving drift-prone droplets into the plant canopy. In application, a common height above the crop canopy is 18 inches (0.46 m). Thus, a 10 µm diameter droplet will probably evaporate before the droplet reaches the canopy if the air is still, and as droplet size decreases, the droplet becomes more susceptible to drift because it will take it longer to travel the remaining distance to the target surface. Thus, some wind is beneficial because the small droplets are moved into the plant canopy, which prevents these droplets from becoming driftable.

It should be noted that atomized droplets are not in still air, and are often traveling faster than their terminal velocities near the nozzle. Droplets then slow down to their terminal velocity due to friction. Also, because the bulk liquid is, on average, traveling into the crop canopy, there is considerable air movement into the crop canopy, especially with high volume (934.6 to 9346 liters per hectare = 100 to 1,000 U.S. gallons per acre) application strategies. Thus, the values in the table should not be used too literally. While it might be nice to provide more accurate values, such calculations are difficult (maybe impossible) due to the number of variables that must be accounted for both in terms of the physico-chemical nature of the sprayed liquid and the external environment.

Many adjuvants added to tank mixtures modify one or more atomization parameters. Such adjuvants include anti-evaporants, spreaders and drift reduction agents. Anti-evaporants retard water loss, thereby increasing the life expectancy of droplets. Anti-evaporants have the greatest effect on smaller droplets. Anti-evaporants may retard water loss by forming a film, or they may be hygroscopic. Spreaders are surfactants. By lowering surface tension, the liquid has less cohesion and breaks apart more readily. Drift-reduction agents are usually polymers. The addition of a polymer increases the viscosity of the liquid, thereby increasing droplet size and reducing the proportion of smaller droplets in the spray cloud. The addition of surfactants and drift control agents may also change the atomization characteristics of the liquid.

Much of the above discussion on atomization is based on the atomization of pure water, or water and a water-soluble formulation. Additional problems arise when the toxicant is dissolved in oil (as in emulsifiable concentrate [EC] formulations) or is left as discrete particles that are suspended in water (as in suspension concentrate [SC] formulations). As an example, consider the SC formulation. During atomization, droplets with diameters less than the particle size of the formulation cannot have any toxicant (assuming the toxicant is completely insoluble, or non-functional if particles are damaged as is the case with the application of an insect pathogen). On the other hand, particles will carry some water with them and some particles will group together to form larger droplets. Consequently, the presence of particles will decrease the numbers of droplets with diameters less than the particle size of the formulation. The distribution function for the numbers of particles based on the size of the droplets will determine the toxicant distribution over the treated surface, and this distribution will influence the biological effect.

Following atomization, the droplets must travel to the plant canopy. They have a velocity vector along the z-axis, and a radial component away from the z-axis is also present in most droplets. Furthermore, the traveling speed of the nozzle over the crop canopy will add a velocity vector that is almost parallel to the y-axis (the exact orientation being determined by the orientation of the nozzle axes on the spray boom). Turbulence from wind passing over the crop canopy and turbulence from the spray boom moving over the field will change the velocity vector of droplets before they impact the plant surface.

The air flow at the plant surface is essentially stationary. The depth of this stationary layer is determined by leaf surface topology. Wind velocity increases gradually until it reaches the current wind speed above the crop. The transition zone between the stationary air and the current wind speed is termed a boundary layer. The boundary layer has no specific dimensions except those defined by the researcher. The direction of air flow in the boundary layer changes from the current wind direction to become almost parallel to the leaf surface (laminar boundary layer). The depth of the laminar boundary layer increases with distance from the leading edge of the leaf. However, temperature gradients, leaf topology and turbulent air flow within the crop limit the size of the laminar boundary layer.

Air flow above the crop canopy is usually turbulent due to interactions between the air mass above the crop and the irregularities within the crop. Furthermore, heating of the ground and crop surface creates convective cells that also contribute to air turbulence above the crop. If temperature gradients are small and the surface is fairly regular (same species, same height, etc…), then the average velocity will increase logarithmically with the height above the canopy until it reaches the wind speed. The depth of the boundary layer above the crop where the air velocity is increasing to the wind speed is a function of the distance traveled over the crop. This is similar to what happens at the leaf-air interface, but the mathematical relationships differ considerably.

The air flow over the crop and over surfaces in the crop canopy are important because droplets must pass through these layers before they impact the plant surface. Droplets that eventually impact a leaf surface must pass through a turbulent layer of air above and within the crop canopy, and then pass through a boundary layer close to the leaf surface where the air movement is laminar and parallel to the leaf surface. Small droplets (usually less than 100 μm diameter) may be carried in the air currents in the laminar boundary layer unless they have sufficient energy to penetrate this layer. These droplets may then deposit on the underside of the leaf if the turbulence at the leeward edge is sufficient, or they are carried somewhere else. Droplets with insufficient energy to reach the crop may end up drifting to other locations and may become health or environmental hazards. Even if such hazards are not present, such losses represent lost revenue to the farmer because the toxicant is no longer in a location for effective management of pest problems in the field.

Impaction and retention

Three physical properties of liquids that are important in relating atomization characteristics to retention on plant surfaces are: 1) equilibrium surface tension; 2) dynamic surface tension; 3) viscosity. Equilibrium surface tension is caused by the cohesive molecular attraction between molecules in the liquid, and molecules at the surface that have one or more sides exposed to the air. Liquids minimize this exposure by keeping the surface area to a minimum, which means that droplets in air will form spheres. Molecules at the surface tend to be more tightly packed and are arranged more regularly than those in the bulk liquid. Equilibrium surface tension is the energy required to expand the surface area of a liquid at rest. When a liquid is moving, the molecules at the surface are less ordered and more similar to the molecules in the bulk liquid. For water, it takes about 40 milliseconds for the surface film to become stable. This period of adjustment is characterized by declining surface tension. Because the surface tension is constantly changing during this period, it is termed dynamic surface tension. Viscosity is also a function of the cohesive forces between molecules, but it also depends on molecular shape. Viscosity is a measure of how readily molecules pass one another. High viscosity may be due to high cohesion between molecules, or because molecules become entangled with one another.

Once the spray cloud reaches the plant canopy, the foliage acts as a filter that removes droplets from the air column. The leaves and stems fill an area through which the droplets will pass aided or hindered by their original velocity following atomization, gravity, friction with the atmosphere and air turbulence. As foliage density increases, the degree of penetration into the canopy will decrease. Furthermore, spray deposits will be greater on surfaces directly facing the nozzle. Usually this is the upper (adaxial) leaf surface, though bent leaves and the flexing of leaves due to air turbulence may result in specific examples where the abaxial surface receives more toxicant. As a general rule, larger droplets will penetrate the plant canopy more effectively than smaller droplets, but smaller droplets have a greater potential to deposit on the bottoms of leaves. The reason is that small droplets are entrained in the laminar air flow around the leaf and are subsequently deposited on the abaxial surface by the turbulent air flow at the edges of the leaf. This results in a common abaxial leaf surface deposit pattern of more droplets occurring at the edge relative to more central abaxial leaf areas.

Impaction occurs when the droplet has penetrated the boundary layers around the leaf and hits the leaf surface. Droplet deformation occurs upon impact with any surface (leaf, leaf hairs, stems, soil, etc.). Droplets spread upon impact, where the degree of spread is a function of the energy of impact balancing with the cohesive forces within the droplet. If the energy of impact is too great, the droplet will shatter into several smaller droplets. If the droplet does not shatter, it will deform into a torus. Dynamic surface tension will pull the torus back into a sphere and the droplet will rebound if it has not adhered to the plant surface. The impact of a droplet upon a surface, its deformation and subsequent rebound (if that occurs) takes about 1 millisecond.

A plant surface consists of several elements important to the retention of droplets. The physical topology of the leaf is defined by the shape of the leaf, folding or bending of the leaf surface, leaf hairs, stomata, the presence of specialized tissues like veins or glands and the shape of the individual cells within these tissues and how they fit together. Leaf shape determines how far air currents travel from the windward to the leeward sides of the leaf. Leaf hairs may increase retention of droplets, but may also prevent droplets from touching the leaf cuticle. Stomata provide a direct route through which insecticides may enter, but only if the surface tension is low enough to reduce the contact angle below the wall angle of the stomata. While this may be desirable for systemic insecticides, it may reduce the biologically available dose for other insecticides. Veins provide channels that may reduce the liquid carrying capacity of the leaf by providing routes along which liquid flows. The spaces between cells also are recessed relative to the intracellular areas. Liquid often becomes trapped in these areas, thereby promoting retention (Figs. 2, 3).

The physico-chemical property of the plant cuticle also plays a role in retention. Plant cuticles are a thin continuous covering that may be from less than 0.1 to 10 μm thick depending on the species and the location on the plant. The outermost two layers are an epicuticular wax layer that blends into the cuticular wax layer. These layers are attached to the cell wall by a matrix of cutin (a cross-linked polymer of hydroxylated fatty acids) and carbohydrate fibers. Below the cell wall is the cell membrane. The physical characteristics of the epicuticular waxes provide the first barrier to retention. The physical structure of this layer is often crystalline, as plates, tubes, rods, or other shapes. These shapes rise above the cuticular waxes and repel water by their physical structure. The epicuticular waxes are mostly composed of long chain (often C_{26} or C_{28}), even numbered, primary alcohols, acetates, aldehydes and fatty acids. Additionally, this layer has odd-numbered (usually C_{29} or C_{31}) alkanes. Additional components are present, though in lesser amounts, and the exact composition is species-specific as modified based on abiotic conditions (e.g., temperature, humidity, light). Thus, the problem for pesticides is to stick to the plant surface. However, contact insecticides cannot stick too well to the plant surface because they must adhere to the insect cuticle. Systemic insecticides also present a special problem because they must pass through these cuticular layers and then be transported in the phloem/xylem. Penetration rates through the cuticle will be dependent on the molecular size of the toxicant, and the path length through the cuticle. Because the cuticle is partly composed of cutin and other long chain organic molecules, toxicants must move around these molecules to penetrate the cuticle. Therefore, the path length is greater than the liner thickness of the cuticle (Fig. 4).

Given the physical and chemical composition of the cuticle, the impacting droplet will remain on the surface if the kinetic energy of the droplet is less than the adhesive forces keeping it on the plant surface. If the droplet has wetted the plant surface upon impaction, some portion of the droplet will remain. Droplets with considerable kinetic energy that have adhered to the plant surface may shatter, giving rise to one or more smaller droplets. Droplets that hit a pre-wetted surface may also provide enough energy to produce one or more smaller droplets. These droplets may impact other plant surfaces, or be lost from the crop. The likelihood that droplets will rebound from a surface or shatter upon impact can be modified with the appropriate selection of stickers, polymers and surfactants. The selection of product must balance drift, impaction and retention. While these products will influence the final distribution of the toxicant, the toxicant distribution will also influence the biological effect of the application. However, in many cases, there is a period of time between the retention of the liquid on the plant surface and the time when the insect encounters the toxicant. During this time, several dynamic events take place that influence toxicant distribution as encountered by the target (or non-target) insect.

Redistribution and deposit formation

Once the liquid spray has settled on the leaf, the deposit finishes spreading over the leaf. The maximum spread is related to the viscosity, surface tension and chemistry of the liquid along with the chemical and physical structure of the plant surface. However, the rate of spread will be inversely proportional to time. Thus, in some cases, droplets will not achieve their maximum dimensions because they do not achieve equilibrium before evaporation reduces the liquid volume. Alternatively, some sprays will contain lipophylic components that may continue to spread through the cuticular wax layers until a steady state has been reached. While it is easy to see an oil spread on waxy plant surfaces, the spread of the lipophylic components is not representative of the spread of the toxicant (Fig. 5).

Droplet size interacts with evaporation to change concentrations within the droplet. Small droplets with a dilute surfactant solution may have insufficient surfactant to wet the leaf surface. Such droplets will evaporate, and the final microscopic piece of formulation and toxicant will be easily dislodged from the surface. Larger droplets of the same solution will maintain a large contact angle with the plant surface until the surfactant concentration reduces surface tension to the point where the surface is wetted.

Under some conditions, the leaf surface could be viewed as a thin layer chromatography plate, and the formulation components as solvents for the toxicant. If the toxicant is nearly insoluble in the formulation, then most of the toxicant will remain wherever it was deposited following atomization. However, if the toxicant is soluble, it will flow over the cuticle with the bulk liquid, and then be carried some distance further as the solvent moves through the cuticular waxes.

The final shape of the deposit after spreading and evaporation have finished is highly variable, and subject to the physico-chemical parameters already discussed. On a flat leaf surface, droplets can form deposits that look like atolls (a ring of small islands located near the outer edges of the droplet), archipelagoes (irregular islands randomly located within the boundaries of the old droplet), mountains (a hill where the formulation components went out of solution, usually near the center of the old droplet), solid films that may or may not cover underlying features of the cuticle, and various other shapes.

Degradation

During these processes, and throughout the life of the toxicant, the toxicant will degrade. Degradation is a combination of a large number of forces that can be classified as chemical or physical. The two most common chemical actions are hydrolysis and photolysis. Hydrolysis is the addition of water to the toxicant molecule. This usually splits the toxicant into two inactive molecules. Photolysis is the action of sunlight hitting the toxicant and breaking it. Within the plant (for systemic toxicants), and within the insect, enzymatic degradation will become more important, but the toxicant has not yet entered the insect or the plant. Physical degradation of the deposit is an abiotic process whereby the toxicant is physically removed from the plant surface. Rain is a common source of physical degradation, but heavy dew or fog can also act in the same manner. For water-soluble toxicants, dew can also redistribute the toxicant over the leaf by rewetting deposits. Wind and wind-blown sand can provide mechanical abrasion to remove surface deposits. While not commonly considered, gutation (exudation of water from leaves due to water pressure from the roots) could also provide sufficient leaf surface water to redistribute toxicants.

The physical forces in toxicant degradation can also act to redistribute the toxicant within the plant canopy. For example, rain may pick up some portion of the toxicant on a leaf surface and move it to the leaf axil, or along the stem. Water that does not fall off the plant will then evaporate creating a new deposit.

Toxicant acquisition and biological result

Following deposition on the plant (or other) surface, the toxicant must be acquired by the insect in sufficient amounts to produce the desired result. Complicating factors include growth of the insect because the lethal dose is determined in part by insect biomass.

Consider a caterpillar feeding on a leaf treated with sufficient toxicant to kill the larva if the larva consumes the entire deposit. If the toxicant is spread uniformly over the entire leaf surface (as might happen if sufficient surfactant is added), then the larva must consume the entire leaf before acquiring a lethal dose. During this time, the larva is exposed to sub-lethal doses, and exposure to sub-lethal doses is one factor that can lead to insecticide failure. Furthermore, the entire leaf has been eaten, so the level of plant damage is high. One solution is to increase the dose of toxicant, but for every doubling of the dose, the savings is only half of the leaf eaten by the larva at the next lower dose; i.e., double the dose from the previous example, save half the leaf, quadruple the dose save three-quarters of the leaf, and so forth. An alternate solution is to concentrate the toxicant into a single deposit. In this case, the larva will (on average) eat only half the leaf. However, in this case there is no benefit to increasing the dose unless there is an accompanying increase in the size of the deposit. This is because the biological response is driven entirely by the probability that the larva will encounter the dose. The benefit is that for a minimal dose, more of the plant is saved and there is no exposure to sub-lethal doses. Obviously, “real” applications produce deposit structures somewhere between these two extremes.

Deposit structure is defined as the distribution of toxicant over a surface. It can be relatively uniform, absolutely uniform, or heterogeneous. Relative uniformity is scale specific, i.e., uniform at 1 cm or greater scales; for example, the ink distribution in a picture in the newspaper. Absolute uniformity is scale independent (at least down to the sub-micrometer level); for example, the distribution of silicon over a computer microchip. Thus, absolute uniformity implies relative uniformity, but the reverse is not true. This is important in application technology because one measure of uniformity is coverage, where the goal of some applications is 100% coverage. 100% coverage may be uniform over a hectare or a whole plant, but is seldom uniform over every leaf on that plant. Absolute uniformity thus implies 100% coverage, but the reverse is not true. Other ways of viewing absolute uniformity is that all toxicant molecules have the greatest possible distance between them over the treated area. Deposit structure can also be heterogeneous. While there are many texts describing heterogeneity in different fields of research, there is no currently accepted measure for heterogeneity in pesticide application.

Two examples will suffice to demonstrate how insect behavior interacts with heterogeneous deposit structures to influence the biological result:

1) If the deposit applied to the leaf surface is sufficient to kill the larva, and the deposit is large enough so that it takes two bites for the larva to ingest the entire deposit, then the way in which the larva feeds will determine the survival time of the larva and the amount of damage to the leaf. At the extremes, a larva could start in one place and feed until all the food was consumed (called ‘chompers’), or a larva could take one bite, move, take another bite, move, and so forth (called

‘nibblers’). With chompers, the larva is most likely to consume the entire deposit once it has encountered it. Thus, on average, the larva will eat just slightly more than half the leaf before it dies. With nibblers, it is unlikely that the larva will eat the second part of the deposit in the bite following acquisition of the first part. Depending on how the larva moves, it may eat half the leaf before encountering the deposit for the first time, and then eat half of the remaining leaf before encountering the deposit again. Thus, the feeding behavior of individuals interacts with heterogeneous toxicant distributions to influence the biological result.

2) If three lethal doses of toxicant are applied as three deposits and three larvae are allowed to feed on the leaf, the result is dependent on whether feeding is sequential or simultaneous. If feeding is sequential, then the first larva will eat 1/2*1/3 of the leaf, the second will eat 1/2*((1-1/2*1/3)/2), and the third will eat half of what is left – thus, 37/48ths (a bit over 3/4) of the leaf will be eaten. If all three larvae feed sequentially, then each larva will feed on its 1/3 of the leaf and consume half of that before encountering a deposit – thus, half the leaf will be eaten. Of course, there are many assumptions necessary to make this simple model work. A few of these are: larvae do not interact, larvae are not cannibalistic, deposits are far apart, larvae die upon consuming the deposit, contact with a deposit does not elicit a behavioral response in the larvae, and the toxicant is only acquired through feeding. Obviously, few larvae interact with toxicants in this way. However, modeling more complex systems can be done by judicious modification to the simplified model.

This approach identifies expected results based on one (or a few) larvae interacting with very well defined deposits. However, many toxicants do not behave in this way (consider a toxicant which acts through inhalation). Furthermore, it requires a careful set of experiments to identify “lethal dose” and care must be taken because the definition of “lethal dose” will change based on how the insect encounters the toxicant. If the toxicant is uniformly distributed, the lethal dose may be quite high because the insect has time to metabolize the toxicant and it can grow. If the toxicant is concentrated, the effect of metabolism is minimized, but the insect will have a variable length of time to grow depending on how long it takes before the toxicant is encountered. An alternative approach is to model the system based only on the characteristics of the droplets used to create deposits on the leaf surface (Fig. 7).

In an atomized spray, the total quantity of toxicant applied to a leaf is related to the number of droplets that are retained by the leaf, the diameter of those droplets (volume = $4/3\ \pi$ (droplet radius)^3), and the concentration of toxicant within each droplet. In an ideal world, all droplets can be considered to have the same toxicant concentration (uneven tank mixing and evaporation rates may change this under actual conditions, but that adds additional complications). Clearly in this system, if the toxicant load on the leaf remains constant, then a change in toxicant concentration must be compensated for by changes in droplet number, droplet size, or both factors. While still a novel approach, recent experiments suggest that the optimal distribution of toxicant is a balancing act between these factors.

Thus, smaller droplets increase efficacy up to a point. This point is reached when the accompanying increases in droplet number provide excessive uniformity, or when accompanying increases in concentration no longer have any effect. Increases in concentration may not have an effect if they do not result in additional toxicant transferred to the target, or (especially with herbicides) the toxicant produces localized damage that restricts further acquisition of toxicant. Likewise, increases in concentration (as with ULV application relative to high volume applications) will improve efficacy until accompanying changes in droplet size or droplet number change the encounter probabilities and thereby reduce toxicant efficacy. By extension, reducing the numbers of droplets will increase toxicity up to the point where reductions in efficacy from suboptimal values of droplet size and toxicant concentration overcome further benefits from using fewer droplets (Fig. 8).

The four variables (dose, droplet number, droplet size and toxicant concentration) define much of the dispersion of toxicant over a leaf surface. If the method of application ensures that the number, size and location of droplets impacting the leaf is random (and toxicant concentration is uniform), then this would be sufficient to define the toxicant distribution over the leaf. However, the distribution of droplet sizes is not uniform within the spray pattern in the x-y plane. Also, large droplets create a wake that can capture smaller droplets. Further, droplet spread, evaporation and the coalescence of droplets are not independent of droplet size. It is, therefore, possible that the models predicting toxicant effects would be improved by including some measure of dispersion. Defining the proper measure of dispersion is still being researched (Fig. 9).

This discussion may make the dose transfer process appear like a very ordered set of linear steps that result in a biological result. However, the process is not entirely linear. A droplet that shatters on impact may hit the ground and be lost, or it may impact the underside of another leaf. If the target insect typically lives on abaxial leaf surfaces, this may improve efficacy. A deposit may be encountered by a non-target insect and moved to another part of the leaf where it may be more (or less) effective. If the deposit contained insufficient toxicant to kill the insect, it could produce a behavioral change in the insect. This behavioral change would then influence the probability of further contact. Also, while it is important to understand how toxicant distributions influence the fate of individual targets, the effect this has on populations should not be ignored. For example, if sublethal doses are common for the population, expect the population to become less susceptible to the toxicant. Sensitive individuals are selected against, and resistant individuals survive to breed the next generation.

This discussion on the dose transfer process is focused on insects and insecticides. However, much of it is important to other pesticides. Most of the material about deposition on surfaces came from research on herbicides, but will also apply to fungicides. The description of the biological effect is specific to insecticides, but with judicious modification, will also apply to some herbicides and systemic fungicides. Because the driving force in many systemic products is a function of the area of contact between the toxicant and the plant surface along with the concentration gradient of the toxicant, there is clearly a tradeoff between increasing the contact area (larger droplets and higher application volume) and increasing the toxicant concentration in the spray tank to achieve a greater concentration gradient. While it is possible to have both of these factors increase by increasing the quantity of toxicant applied, such an approach is environmentally unfriendly and not an economically viable option for farmers.

The importance of insect behavior should not be underestimated. Behavior reflects toxin apparency, mode of action, and insect response to sublethal doses. The interaction between these behavioral responses and heterogeneously distributed toxins and physiological mechanisms of tolerance may influence the evolution of insecticide resistance.

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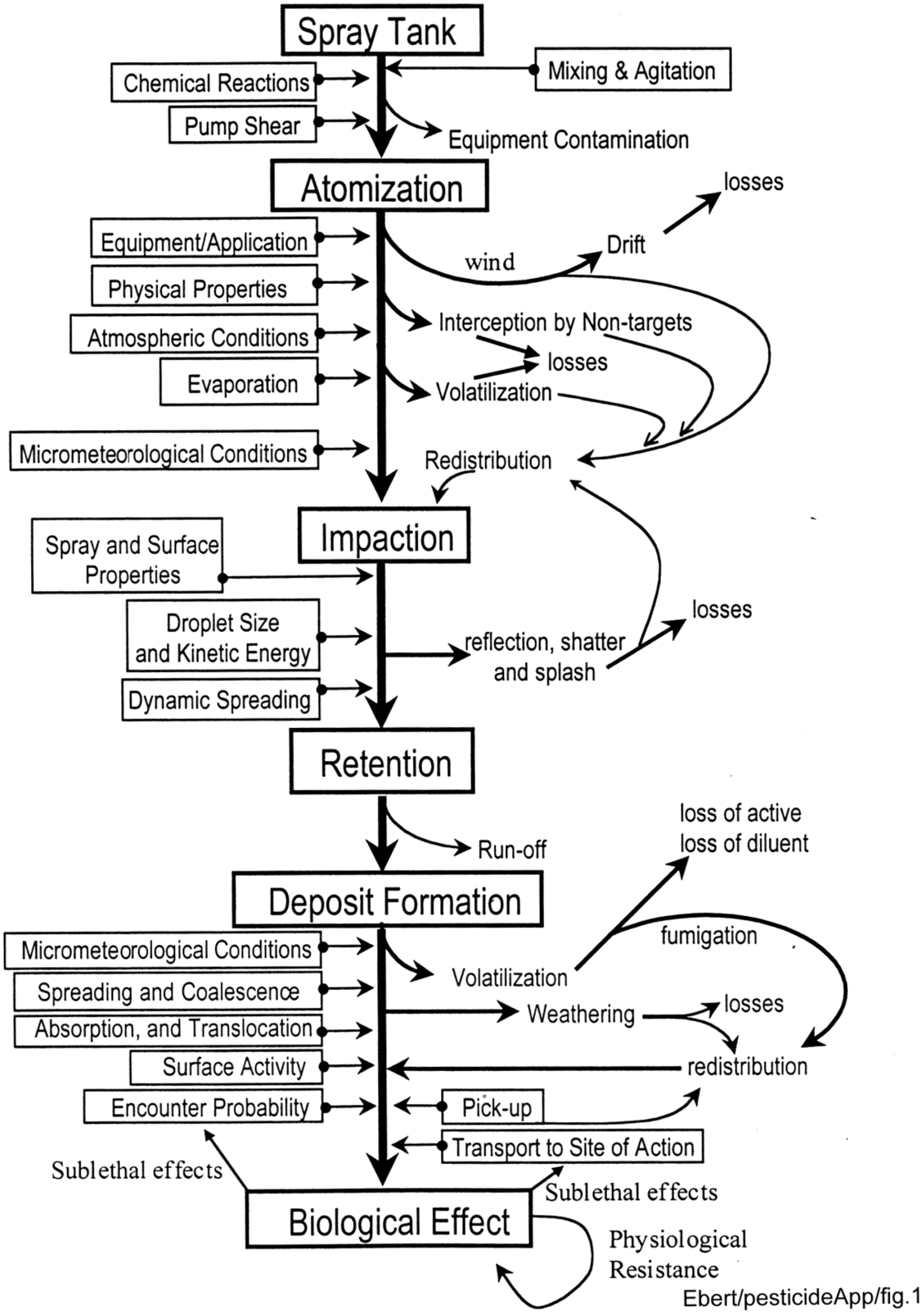

Ebert/pesticideApp/fig.1

Figure 1. Flow diagram representing application of liquid pesticide.

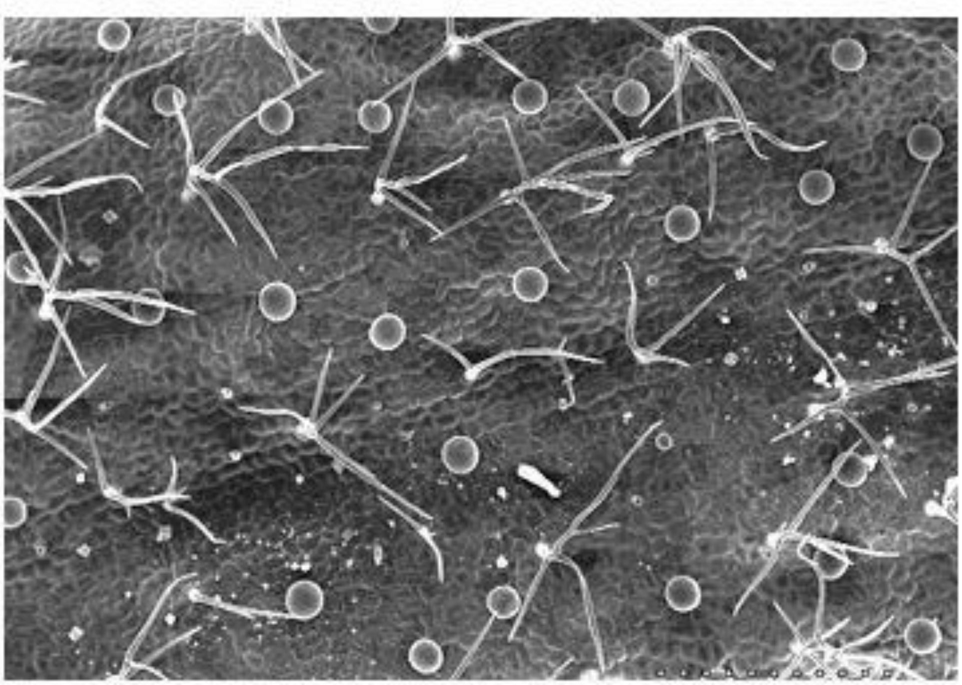

Figure 2. The adaxial surface of a rosemary leaf. The circular objects are glands. The leaf has a little bit of dirt that has splashed onto the leaf surface.

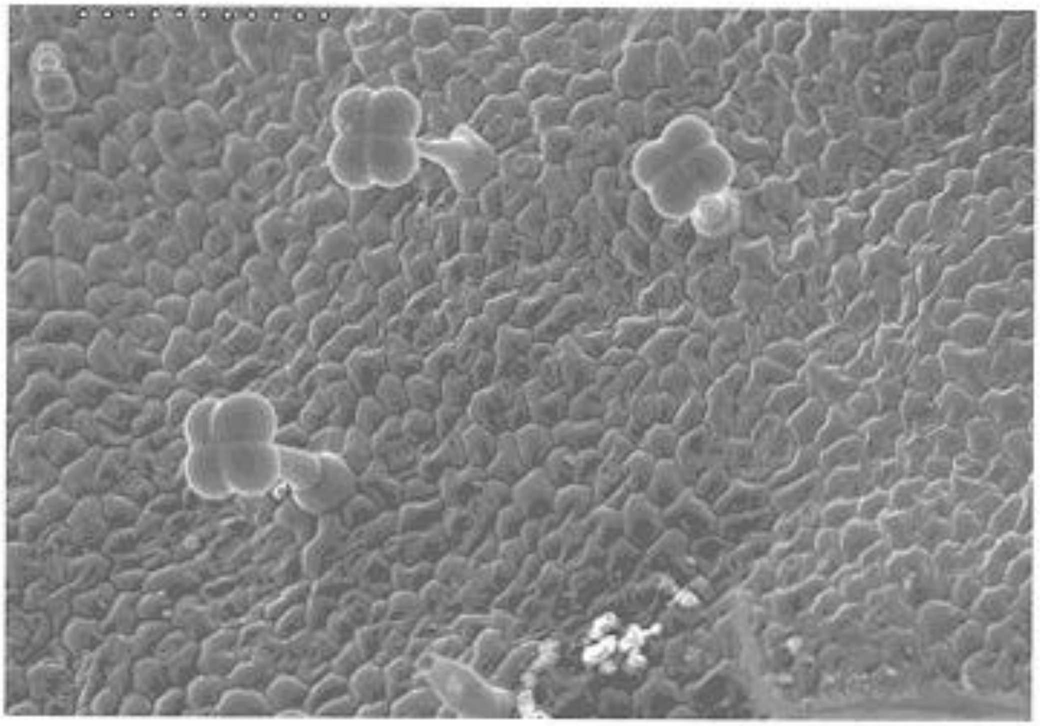

Figure 3. The adaxial surface of a tomato leaf. The 4-lobed glands are on stalks.

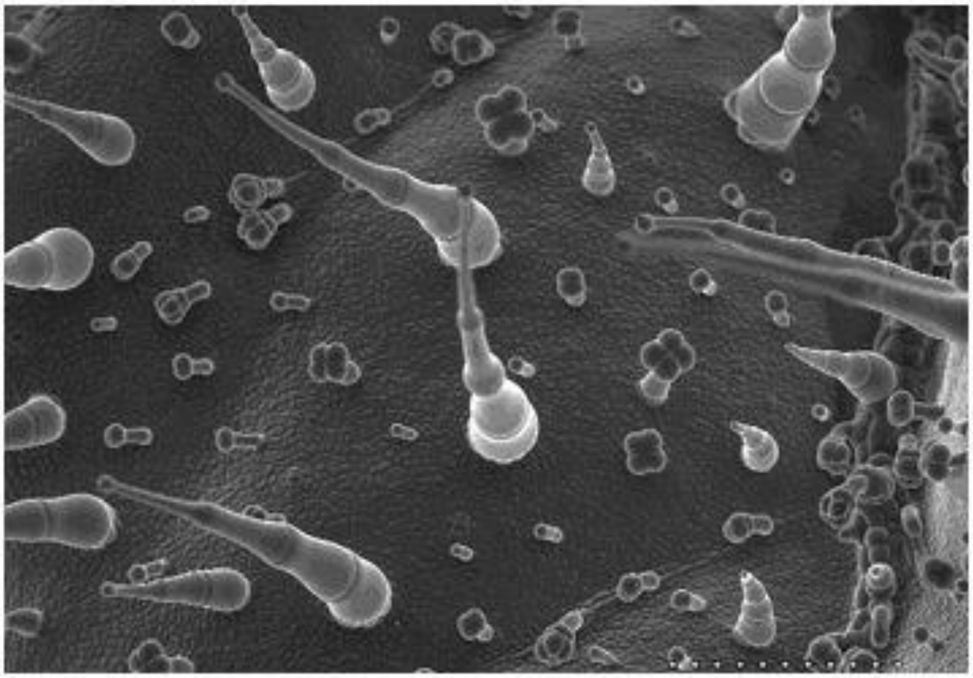

Figure 4. Glands and hairs on the adaxial surface of a young tomato leaf. Glands may be 4-lobed or simple.

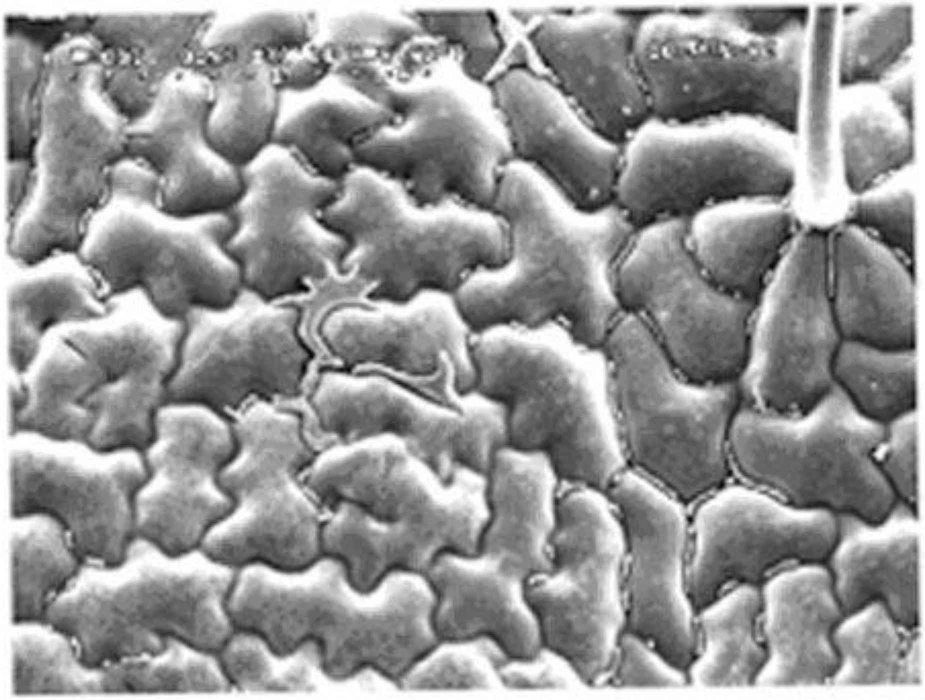

Figure 5. Roundup Ultra sprayed on the adaxial surface of a cotton leaf. The deposit has filled in the gaps between cells.

Figure 6. The DRAMM Coldfogger sprayer for greenhouse pest management. The sprayer delivers a fine mist under high pressure.

Figure 7. The Electrostatic Spraying Systems Inc. EPS-5 sprayer. The sprayer delivers a fine mist that is electrically charged and forced into the canopy by compressed air.

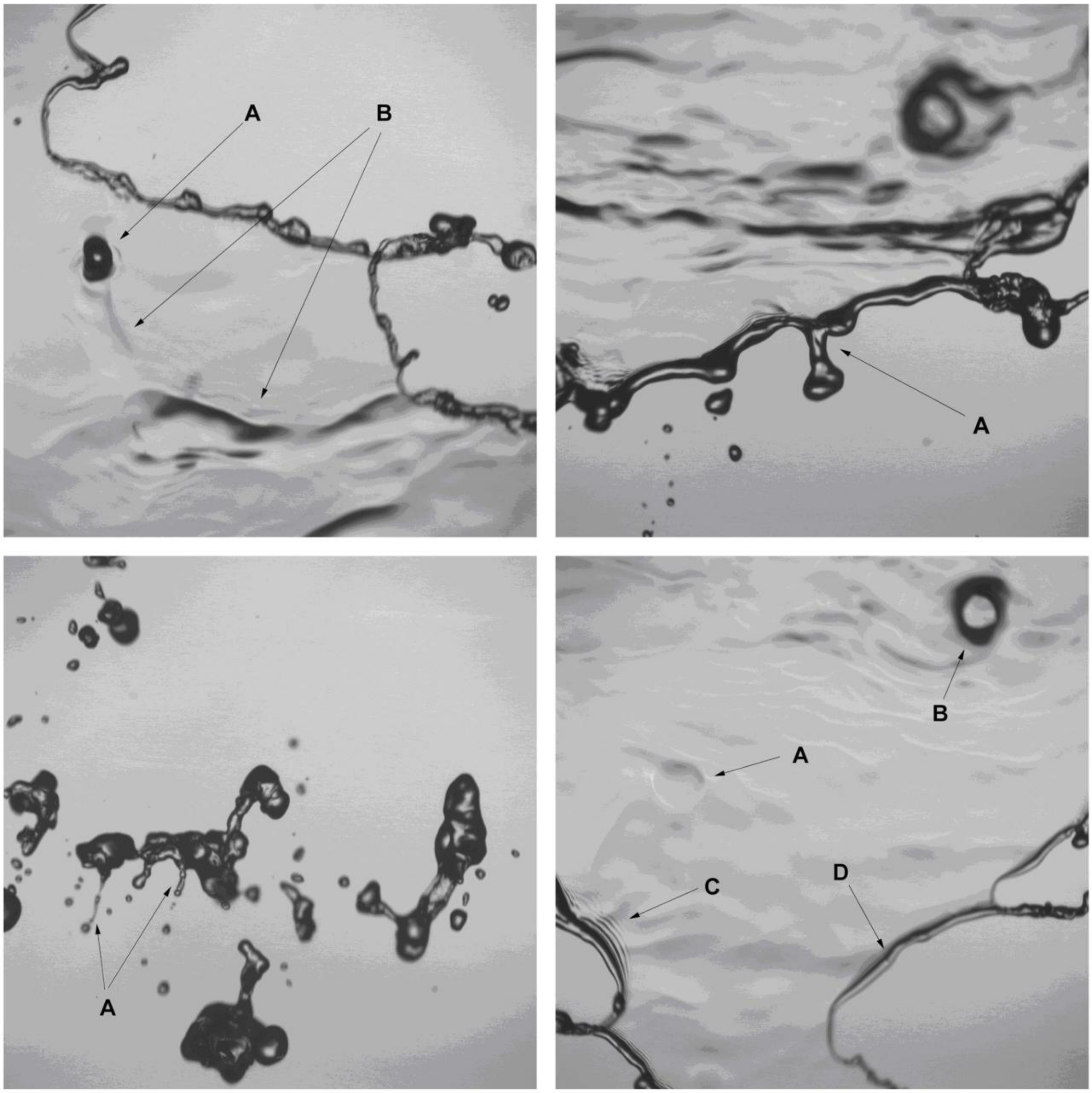

Figure 8. Wavy sheet disintegration. Each picture is a 9.4 mm^2 area of the disintegrating liquid sheet produced by a Spraying Systems AI110015 nozzle. Pictures taken with an Oxford Lasers Visisizer. 1: Sheet disintegration, (a) hole formation, (b) waves in the sheet. 2: Ligament formation, (a) ligament between sheet edge and forming droplet. 3: Secondary droplet disintegration, (a) ligaments and droplets developing from larger unstable droplets. 4: Disintegration from holes in the sheet also produces droplets, (a) a developing hole that has not yet perforated the sheet, (b) a hole in the sheet, (c) shock waves at the edge of the sheet, (d) thickened edge. (Photos by Timothy Ebert and James Hacker and courtesy of Laboratory for Pest Control Application Technology.)