

## CHAPTER 1: INTRODUCTION AND JUSTIFICATION

Loblolly pine (*Pinus taeda* L) is the leading Southern (USA) pine, in terms of acres planted, (Fortson *et al.*, 1996). As the resource base has grown, so has the interest in intensive management of the species. Prior to 1960, often the only site preparation was a burn. In the 1960s and 1970s, most plantations were established following some type of mechanical site preparation (chopping, root raking, harrowing, etc.). Even very intensive and expensive mechanical site preparation treatments did not eliminate many of the hardwood competitors. As a result, a considerable acreage of young mid-rotation age loblolly pine plantations in the southeastern United States has a substantial hardwood component (Fortson *et al.*, 1996). Hardwoods on cutover lands usually develop from root and stump sprouts which grow vigorously and compete aggressively with planted pines. Control of hardwoods in young loblolly pine stands (release) is an option that has resulted in positive pine growth responses within a few years of treatment ( Bacon and Zedaker, 1987; Zutter *et al.*, 1988; Glover *et al.*, 1991). Miller *et al.*(1991) compared complete woody control to complete herbaceous control at 13 locations and found that at age 5, herbaceous control increased pine volume more than woody control at all but one location. In contrast to herbaceous weeds, however, uncontrolled hardwoods continue to compete aggressively with pines throughout a rotation, especially when hardwoods remain in the pine canopy. Hardwoods can have a disproportionately larger effect on loblolly pine growth than intraspecific competition between loblolly pine trees (Liu and Burkhart, 1994).

Competing vegetation can be efficiently controlled by herbicides, which need to be formulated either in-can or in-tank to allow them to perform optimally. Adjuvants have proven essential to increasing the efficacy of herbicides, due to their ability to consistently improve the performance of the basic pesticide product. The Weed Science Society of America (1983) defines an adjuvant as "any substance in a herbicide formulation or added to the spray tank to improve herbicidal activity or application characteristics". Another definition of adjuvants has been "any non-pesticide material added to a pesticide spray mixture to improve chemical or physical characteristics"(Helena Chemical Company, 1988). The most important reason for the use of adjuvants is their ability to improve the performance and consistency of the basic pesticide

product. There are, broadly speaking, two routes by which adjuvants can do this. The first is the minimization of off-target deposition and second by the maximization of the herbicidal effect once it is deposited on the target (Reeves, 1989). The major contributors to off-target deposition are drift, in-flight volatilization, droplet shatter, bounce or runoff, washoff, and removal by wind. These losses result in pesticides never reaching the target or achieving only transitory deposition.

There are two basic methods of maximizing the effect of the pesticide once it is on the target. The first is to improve coverage by the spray solution, which can be accomplished by lowering the surface tension of the spray with surfactant materials. The second is by improving the penetration or uptake into the target. Organosilicone surfactants can reduce the surface tension of aqueous pesticides far below that which is possible with nonsilicone surfactants, resulting in efficient wetting of even the most hydrophobic leaf surfaces. Additionally, by virtue of their low surface tension, these adjuvants can significantly increase the uptake of active chemicals directly into the plant via stomatal infiltration (Stevens *et al.*, 1991).

Triclopyr ([3,5,6-trichloro-2-pyridinyl]oxy]acetic acid) has been found to be an effective herbicide for hardwood control. Its two commercial formulations, a triethylamine (TEA) salt (Garlon 3A) and a butoxyethyl ester (Garlon 4), vary considerably in their acceptability. The current ester formulation has two undesirable characteristics. One is that all ester formulations, regardless of chain length, have some volatility which is usually more than that of water-soluble salts. The second is that the current ester formulation utilizes a kerosene solvent which is known to cause rapid foliar necrosis (possibly inhibiting herbicide translocation) and is a suspected carcinogen (Zedaker *et al.*, 1995). In most applications, the ester formulation has been more efficacious than the amine formulation on an equal active ingredient basis. Where equal cost mixtures were tested, again the ester formulation was more efficacious than the amine formulation (Miller, 1988). Research, sponsored by DowElanco, USA and Witco, OrganoSilicones Group, USA and conducted by Virginia Polytechnic Institute & State University and the New Zealand Forest Research Institute researchers over the past few years had demonstrated a substantial potential to enhance the uptake of triclopyr into plant foliage in the presence of organosilicones. The researchers found that the commercial TEA formulation of triclopyr (Garlon 3A) was

"antagonistic" to the organosilicone surfactant Silwet L-77. To take full advantage of the properties of organosilicones, the antagonistic co-formulants of Garlon 3A needed to be removed or replaced, the best surfactant formulation identified, and a cost-effective concentration of the surfactant(s) needed to be established.

To do this adequately required that both physico-chemical processes and biological processes be studied. The relevant physico-chemical processes involved in a formulation's effect on spray impaction on the target plant include adhesion, reflection, retention and run-off. The important biological processes include the uptake and translocation of the herbicide into the plant, the mechanism of uptake eg. uptake via stomatal or cuticular pathways, the rate of uptake, and contact phytotoxicity.

This thesis focused on the physical-chemical processes, with a foray into the biological effects in relation to contact phytotoxicity

The objectives of this study were

1. To evaluate the influence of formulation, active ingredient concentration, droplet size, leaf surface (adaxial vs. abaxial) and time on contact phytotoxicity to *Acer rubrum*, *Liquidambar styraciflua* and *Quercus rubra* by triclopyr formulations containing organosilicone and mixtures of silicone-conventional surfactants.
2. To evaluate the influence of formulation, active ingredient concentration, leaf angle, droplet size and leaf surface (adaxial vs. abaxial) on adhesion and retention of triclopyr formulations containing organosilicone and mixtures of silicone-conventional surfactants, to *Acer rubrum*, *Liquidambar styraciflua* and *Quercus rubra*.
3. To evaluate the influence of formulation and active ingredient concentration on spray retention by the adaxial and abaxial leaf surface of the selected species under field and track-sprayer conditions.

4. To determine whether leaf characteristics (wax character and leaf angle ) could explain adhesion / retention.

## CHAPTER 2: LITERATURE REVIEW

### FORESTRY IN THE SOUTHERN UNITED STATES

The southern forest of the USA occupies land from Virginia to eastern Texas and Oklahoma (USDA Forest Service 1982), with major sub-regions consisting of the Lower Coastal Plain, the Piedmont, the Appalachian Highlands, and the Interior Highlands (Wright and Bailey, 1982). The South is rapidly becoming the nation's leading producer of forest products ( Gjerstad and Barber, 1987). In 1976 the Pacific Northwest supplied 50% of the nation's softwood products, whereas the South provided 36%. By 2030 much of the commercial old growth timber in the Pacific Northwest will have been cut, and it is projected that the South will supply half of the nation's softwood requirement for both pulpwood and sawtimber. The main commercial species are the southern pines, and on a much smaller scale, hardwoods in plantations and natural stands found on bottomland sites. The importance of pine to the region, as well as the nation, is demonstrated by loblolly pine accounting for 60% of the bare-root seedlings planted in the United States (Boyer and South, 1984). In addition, the combined number of loblolly and slash pine bare-root seedlings is more than double all other species planted in the United States. Because commercial forest acreage is predicted to remain fairly constant over the next 50 years, productivity must be increased if the South is going to meet a larger share of the nation's timber supply needs ( Gjerstad and Barber, 1987).

Hardwoods have been shown to have a consistent negative growth impact on pines, and pine diameter growth has been shown to be more sensitive to woody competition than pine height ( Knowe, 1991; Lanner, 1985; Zutter *et al.*, 1986). In a study by Quicke *et al.* (1996), on a hardwood-to-pine conversion area that had been chopped and burned, then analyzed 7 years after treatment, it was found that all broadcast herbicide treatments used on the study were effective in controlling hardwoods, with the least effective treatment decreasing hardwood basal area by 55% relative to the untreated check. The pine crop trees responded with increased diameter, height, basal area and volume. The increase in total pine volume outside bark over the untreated check

ranged from 163 to 640 ft<sup>3</sup>/ac (22% to 85%) and the increase in pine basal area ranged from 13 to 40 ft<sup>2</sup>/ac (27% to 83%).

Glover and Zutter (1993) presented data from a study site in Fayette County, Alabama, where hardwoods and pines had been measured periodically over a 27 yr. time period. They found strong negative relationships between pine basal area at age 27 and both number of hardwood stems at age 3 and percent of stand basal area in hardwood at age 6. Control of competing vegetation has been shown to improve growth of newly regenerated stands and that response is lengthy (Shiver *et al.*, 1990; Haywood and Tiarks, 1990).

Fortson *et al.* (1996) concluded that it was becoming more obvious that older stands also respond to control of competing vegetation and that the magnitude of that response may make competition control in well established stands an economical option for forest managers.

There have also been studies in natural stands to examine the effects of hardwood control (Cain, 1991; D'Anieri *et al.*, 1986), but in virtually every case, the studies were limited to one or two study locations and results often conflicted from one study to another. The objectives of a study by Shiver and Brister (1996) was to evaluate the effect of hardwood and pine density on natural loblolly pine stand yields and product distributions. The difference in product distribution for varying levels of hardwood proportions while holding constant trees per acre, stand dominant height, and total basal area, was studied. As hardwood proportion increased, two things were shown to happen. The overall pine yield decreased and the proportion of yield in sawtimber decreased. The pulpwood and chip-n-saw yields were not changed dramatically when the hardwood proportion of basal area increased. Almost all of the decrease in pine yield came from pine sawtimber. Each increase of 10% in hardwood basal area cost about 20% of the sawtimber volume. A concluding implication for managers in this study was that only very small amounts of hardwood can be tolerated in natural pine stands if the product objective is sawtimber.

Thus hardwood control has been shown to be important not only in the early years of a stands life, but can also lead to increased pine yields when hardwood control is undertaken in older stands, and has been shown to be important not only in plantation forests, but also in natural stands.

In a study by Shiver *et al.* (1990) comparing site preparation treatments, a shear, rake, and disk treatment provided comparable control to chemical treatments in the spring study, but at a higher cost. Double chopping was not an effective treatment in the late summer study. Knowe *et al.* (1992) made the observation that the traditional “site preparation method in the Southeast was some form of mechanical treatment. Increased costs and concerns for maintaining long-term forest productivity resulted in a shift from mechanical site preparation to herbicide treatments that produce less site disturbance. Forest vegetation management with herbicides has also increased because it may provide an opportunity to increase growth with reduced costs”. An effective herbicide treatment would be the most economical way to control hardwoods in the United States.

## **CHEMICAL WEED CONTROL IN CONIFER PLANTATIONS**

The use of chemicals to control unwanted herbaceous and woody vegetation developed as early as 1915 ( Kidd, 1987). Following the discovery of the auxin-like properties of the chlorinated phenoxyacetic acids in the early 1940's, the use of chemicals increased greatly.

For conifer plantation release, a product must adequately retard woody broadleaf plant development without significant adverse effects on conifers. Herbicides are generally conceded to be the most feasible approach for assuring the initial freedom from water and light stress most essential for early survival and success of conifer plantations. Because water loss by evaporation often exceeds gains from precipitation during the growing season (April to October, USA), reducing evapotranspiration by eliminating competing vegetation will result in greater soil water availability to pines. Competing vegetation is usually in the form of grasses and broadleaved weeds during the early years, and woody shrubs and other trees during the later years of stand development. Release applications capitalize on basic biochemical selectivity of the pesticide among species. Growth injury from herbicides is transient in most conifers, when it does not exceed partial defoliation, and growth losses measured after partial defoliation have been minor.

Even the loss of occasional growing tips or leaders does not signify a major loss of growth. These impacts are often more than compensated for by the benefits of crop tree release ( Kidd, 1987).

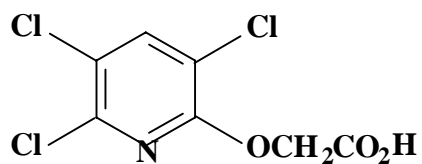
Triclopyr (Figure 1) is a synthetic growth-regulator type herbicide intermediate in many effects between picloram and 2,4,5-T. Triclopyr has been commercially available since the 1970's and is the active ingredient found in Pathfinder and Garlon 4 ( present as the ester in both ), Garlon 3A ( present as the amine salt), and Turflon ( available both as an ester and an amine )( Farm chemicals handbook, 1992). It is effective at certain seasons on broadleaf woody species, primarily through foliar uptake (Newton and Knight, 1981).

The favorable toxicology of triclopyr demonstrates that it may be used for control of woody plants and broadleaf weeds on rangeland, permanent pasture, rights-of-way, and industrial sites over a range of conditions ( Gangstad and Montz, 1989 ). Triclopyr is registered for the control of many broadleaved annual and perennial weeds and woody plants including the species that will be used in this study - maple ( *Acer* ), sweetgum ( *Liquidambar* ) and oak ( *Quercus* ) ( USDA compilation of registered uses of herbicides, Gangstad and Montz, 1989).

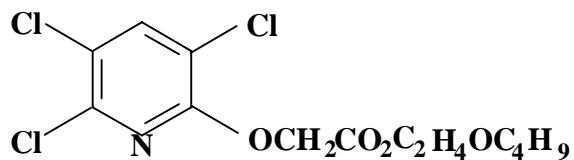
Triclopyr controls species such as aspen and maple better than 2,4-D and it controls maple better than does glyphosate ( Newton and Knight, 1981). Reynolds *et al.* (1983) demonstrated that triclopyr amine was an effective herbicide for killing large diameter Appalachian hardwoods. The results showed that triclopyr amine can be used successfully for managing canopy-crowned and/or tree-overgrown pipeline right of ways. Preliminary results indicated that triclopyr amine may be more effective than triclopyr ester in controlling the growth of large ( up to 24 inches dbh, 60 feet tall) mixed mesophytic hardwoods (Reynolds *et al.*, 1983). However, most subsequent research showed the reverse. Miller (1988) found that with directed sprays hardwood control was greater with Garlon 4 (2%) than with Garlon 3A (2.5%). Miller (1990) found no significant difference between Garlon 4 (2%) and Garlon 3A (2.5%) when used as foliar directed



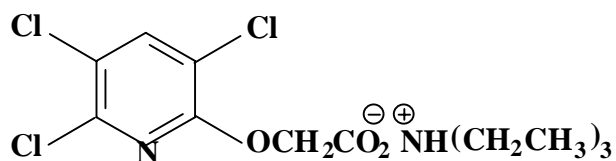
A Triclopyr acid  $C_7H_4Cl_3NO_3$



B Triclopyr butoxyethyl ester  $C_{13}H_{16}Cl_3NO_4$  (oil soluble)



C Triclopyr triethylamine salt  $C_7H_4Cl_3NO_3 \cdot N(CH_2CH_3)_3$  (water soluble)



**Figure 1:** The structural and chemical formulae of triclopyr acid (A), Triclopyr butoxyethyl ester (B) and Triclopyr triethylamine salt (C).

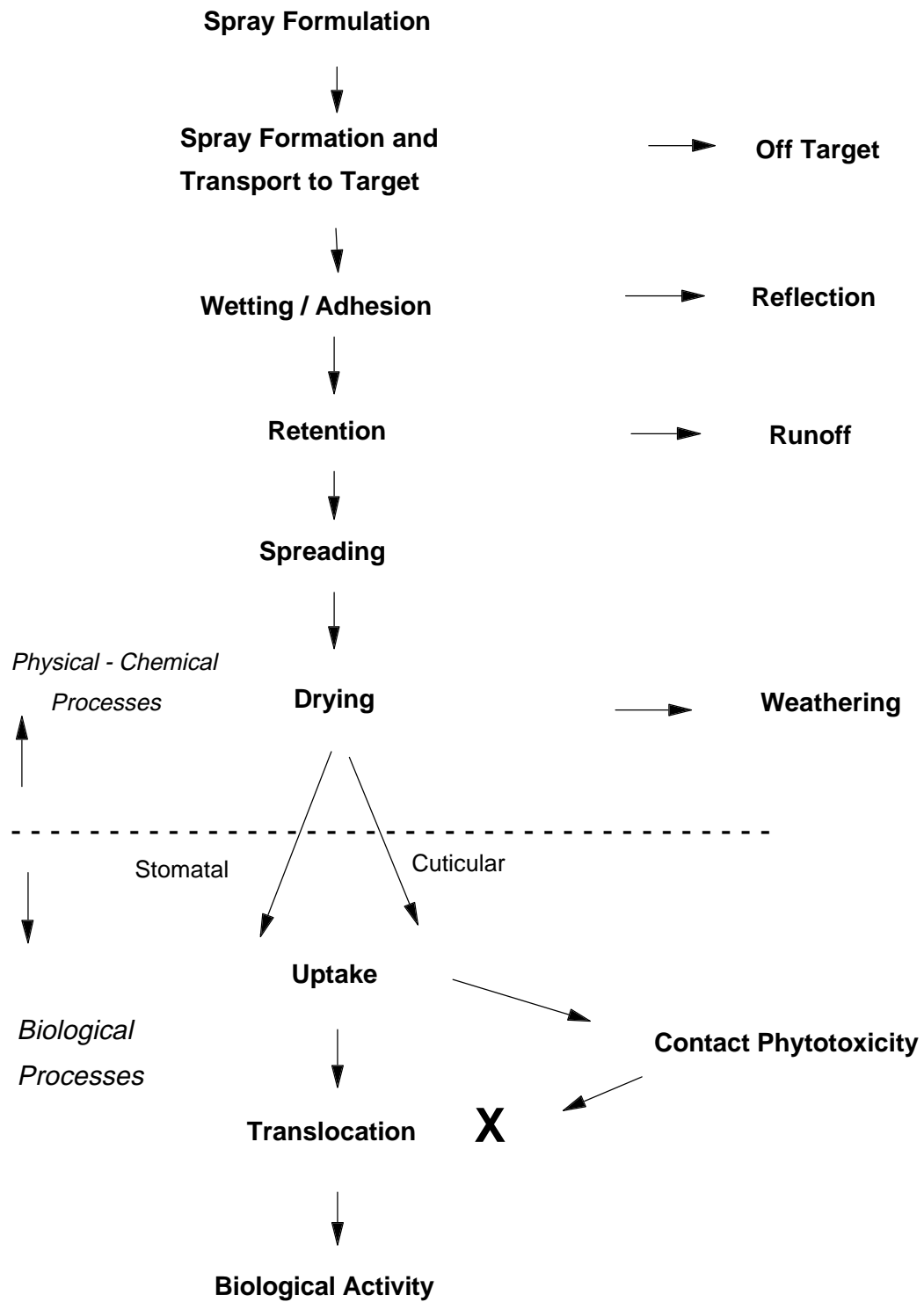
sprays for crown volume reduction against 7 different hardwood species, when the sprays were applied in May and July. However, when the sprays were applied in September, Garlon 4 was found to be significantly better than Garlon 3A at reducing the crown volume of southern red oak and water oak. In a comparison of chemical site preparation treatments in the Georgia Piedmont (Shiver *et al.*, 1990), Garlon 4 herbicide applied in the spring provided better control of dogwood, red maple, and water/willow oak than Garlon 3A herbicide (used on an equal cost basis). Garlon 3A never provided better results than Garlon 4 herbicide. In a study by Yeiser (1997) involving low-volume foliar sprays for rights-of-way cleanup, there was found to be no significant difference between Garlon 4 (3%) and Garlon 3A (4%) for crown reduction of sweetgum, elm and loblolly pine, whereas Garlon 4 was significantly better than Garlon 3A at reducing the percent crown cover of southern red oak and at reducing the herbaceous grasses making up the ground cover. There are known differences in efficacy of both the ester and the amine formulation (Miller, 1990; Yeiser, 1997) against different target species; alternative formulations may overcome these species differences.

## **FACTORS AFFECTING HERBICIDE EFFICACY**

Most pesticides are applied to foliage as sprays of water-based formulations atomized through hydraulic nozzles. It is well known that this method of transfer is inherently inefficient, resulting in only a proportion of the dose applied actually being deposited on the intended target, with even less eventually reaching the ultimate site of biological action (Holloway, 1994). After atomization, up to the active ingredient reaching the site of biological action, there are a number of factors, both physico-chemical (involving transport to and impaction on the plant), and biological (involving uptake and translocation), which contribute to this shortfall (Figure 2).

### **Transport to target**

A major problem with many effective pesticides is the hazard of airborne drift or aerial transport out of target areas. Both public and private agencies have expended considerable effort on reduction of drift through improvement of formulation and application technologies. Hydraulic nozzles and formulations produce a relatively broad spectrum of droplet sizes. One possible way



**Figure 2:** Factors affecting herbicide efficacy

of reducing spray drift is through adjuvants that alter the physical properties of the fluid. Some physical properties may affect the basic atomization process and thereby may reduce the number of small drops ( less than 100  $\mu\text{m}$  in diameter) produced ( Yates *et al.*, 1976 ). Surfactants have been shown (Stevens, 1993) to markedly reduce the volume mean diameter (VMD) of sprays through an 8003LP high-flow, low-pressure nozzle - by over 50% when organosilicone adjuvants were used at relatively high concentration. In contrast, none of the surfactants had an effect on the VMD of an 8001 low-flow, high pressure nozzle. The proportion of the spray delivered in small, potentially driftable droplets ( $< 100 \mu\text{m}$ ) was not increased greatly for the 8003LP. This suggests that these surfactants may be used to advantage with low-pressure nozzles, which are being used increasingly to avoid drift problems, but which produce such large droplets that spray adhesion and coverage may be adversely affected. The results with the 8001 nozzle again were contrasting, with the proportion of spray in small droplets being increasing to unacceptable levels.

This information is very relevant to this study as both the microfoil boom sprayer and the radiarc sprayer are low pressure sprayers producing large droplets. It is possible that the inclusion of an organosilicone surfactant will decrease the size of the droplets produced by these sprayers but not increase the proportion of potentially driftable droplets. However, in the study by Stevens (1993) the concentration of each surfactant was not kept constant, and there was no active ingredient in the spray. This raises questions as to what would actually occur if we were comparing surfactants of the same concentration, and what differences would be seen if the formulation included active ingredient?

### **Wetting / Adhesion**

Spray droplets must be capable of wetting the waxy, water-repellent surfaces of foliage to be retained on the target plant. Wetting is determined as the contact angle that a droplet makes with the surface ( Holloway, 1970). The physical behavior of water-containing droplets when they impact with a solid surface has been documented by high-speed photography and the energy transfer processes involved described in detail (Brazee *et al.*, 1991; Ford and Furmidge, 1967; Lake, 1977; Spillman, 1984; Tadros, 1987; Wirth *et al.*, 1991; Young, 1980 ). Three things may happen depending mainly on the droplet size, the droplet velocity and the intrinsic physico-

chemical properties of both droplet and leaf surface. The droplet may adhere to the leaf surface, be reflected or shatter into smaller satellite droplets which may be lost to the target or undergo further impaction ( Tadros, 1987; Forster and Zabkiewicz, 1994 ).

### **Retention**

When the droplets have adhered to the solid surface, the spray retained increases proportionally with the volume applied until the surface becomes saturated with spray. At this point 'run-off' commences and, on continued spraying, the volume retained tends to decrease ( Furmidge, 1962). Thus the maximum deposit will be formed at the point of incipient run-off . The retention has also been shown to decrease when wetters were added to the spray.

### **Spreading**

A spray droplet deposited on foliage may either maintain its original shape on impaction, spread, or contract. The major factors involved in the eventual outcome are the surface tension of the liquid and the physico-chemical (leaf surface morphology and wax characteristics) properties of the surface. Coverage depends on the volume of spray applied, the structure of the target and the nature of the formulation. Maximum coverage is required for pesticides which have a protectant action, but is probably less important for systemic ones. The organosilicone surfactants' spreading ability is far greater than the majority of conventional surfactants. For example, the spreading ability of the organosilicone surfactant Silwet L-77 is related to its potential to reduce the surface tension of aqueous solutions (  $\approx 21$  mN/m), and to its compact structure ( Goddard *et al.*, 1992). Goddard *et al.* (1992) suggested that the compact hydrophobic portion of the organosilicone surfactant allows it to readily transfer from the air-liquid interface of the advancing solution to a low energy surface, such as a waxy leaf cuticle. This phenomenon is likened to a "Molecular Zippering" of the liquid/solid interface. Similarly, the conventional surfactant is depicted with a large bulky hydrophobe that tends to act like a prop for the advancing droplet. This propping effect causes interference with the spreading of the solution. In short, the "zipper" jams ( Policello *et al.*, 1993).

Another theory for the “superspreading” ability of some nonionic trisiloxane surfactants has been put forward by Venzmer and Wilkowski (1998). They suggest that these surfactants form bilayer aggregates (vesicles, lamellar phases) in aqueous solution, as opposed to forming micelles. When micelle-forming surfactants adsorb on a hydrophobic substrate, hemimicelles are formed. This arrangement forces hydrophilic headgroups into contact with the hydrophobic substrate, an orientation less than ideal for lowering interfacial tension. In contrast, when bilayer-forming surfactants (with a critical packing parameter of  $P \gg 1$ ) interact with hydrophobic substrates, such curved aggregates can not develop; instead a smooth coverage of the substrate has been found. In this case, only the hydrophobic portions of the surfactants are in contact with the surface. Therefore, the interfacial tension at this interface can be expected to be lower than that with micelle-forming surfactants (Venzmer and Wilkowski, 1998).

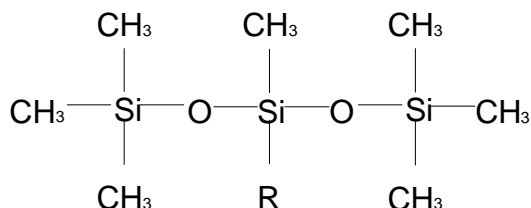
Judicious selection of co-formulants for the organosilicone surfactant is critical when formulating pesticide sprays. The inclusion of some additives can interfere (antagonize) with the spreading properties associated with the organosilicones (Murphy *et al.*, 1991).

### **Drying**

Surfactants can reduce the evaporation of aqueous droplets by adsorption at the liquid/air interface (Hartley and Howes, 1961). In practice, however, once deposited, the rate of evaporation is highly, but not perfectly, correlated with the interfacial area (Zabkiewicz *et al.*, 1988). Thus, in keeping with their spreading, the rate of evaporation of aqueous organosilicones increases with their concentration (Stevens and Zabkiewicz, 1990), and exceeds that of various conventional surfactants (Gaskin and Zabkiewicz, 1989). This has led to some concern because the rate of uptake from drying droplets is much faster than from visibly dried deposits, and quantities of a.i. taken up during droplet drying may be significant (Stevens *et al.*, 1987).

## ORGANOSILICONE & CONVENTIONAL SURFACTANTS USED IN STUDY

Two organosilicone surfactants were chosen by OSi Specialties to be used in this research. They were: Silwet L-77 and Silwet 408 (Figure 3).



Where for Silwet L-77:  $\text{R} = -\text{C}_3\text{H}_6\text{O} - (\text{C}_2\text{H}_4\text{O})_8 - \text{CH}_3$

and for Silwet 408:  $\text{R} = -\text{C}_3\text{H}_6\text{O} - (\text{C}_2\text{H}_4\text{O})_8 - \text{H}$

**Figure 3:** Structures of the organosilicone surfactants Silwet L-77 and Silwet 408

The only difference between Silwet L-77 and Silwet 408 is the EO chain endcap, Silwet L-77 providing a methoxy endcap and Silwet 408 providing a hydroxy endcap. The difference in endcap has been shown to cause differences in physical characteristics.

Gaskin and Stevens (1993) reported that Silwet L-77 antagonized the foliar uptake of glyphosate into grasses whereas Silwet 408 did not. Silwet L-77 was reported to provide higher adhesion than Silwet 408 to the extremely difficult to wet leaf surface of pea (*Pisum sativum* L.) (Stevens *et al.*, 1992).

Organosilicone surfactants have enhanced the efficacy of many herbicide formulations, due to their ability to both increase leaf wetting (Neumann and Prinz, 1974a) and rapidly infiltrate stomata (Neumann and Prinz, 1974b) by virtue of their low surface tensions.

Two excellent reviews have been carried out on organosilicone surfactants in agriculture (Stevens, 1993; Knoche, 1994).

Alkylphenolic glycol ether is the current wetter / emulsifier in Garlon 3A. Research by Virginia Polytechnic Institute and State University and the New Zealand Research Institute found antagonism to exist when used in conjunction with the organosilicone Silwet L-77. An alcohol ethoxylate ( Rhodasurf DA-630) and n-octyl pyrrolidone (Surfadone LP-100) were chosen by DowElanco as other possible wetter / co-surfactants to be used with the organosilicone surfactants. It was recommended that these co-surfactants were used at 1% of product ( Pers. Com. by Nelson Keeney, DowElanco).

### **CHARACTERISTICS OF ADHESION AND RETENTION**

Adhesion has been defined as the percentage of drops adhering on *initial* impact, whereas retention has been defined as the amount of solution ( drops and satellite droplets) remaining on the leaf ( Forster and Zabkiewicz, 1994; Stevens *et al.*, 1993 ). The words of Hartley (Hartley, 1966) are worth noting: 'On a question of terminology, it is a pity that so many different processes are brought, without differentiation, under the heading of "retention". Droplets are first accepted [ i.e. *adhesion* ] or reflected, the accepted drops then spread to varying extent and may fuse, large drops formed by fusion may run off or a completely spread film may drain off ...the proportion of spray *retained*... can be influenced by these largely distinct processes.' When a drop of liquid impinges on a solid surface ( e.g. a leaf) one of several states may arise depending on the conditions. The drop may bounce or undergo fragmentation into two or more smaller droplets which in turn may bounce back and then return to the surface with a lower kinetic energy. Alternatively the drop may adhere to the surface after passing through several stages whereby it flattens, retracts, spreads and finally rests to form a hemispherical cap. In some cases the droplet does not adhere initially but floats as an individual drop for a fraction of a second or even several seconds and can either adhere to the surface or bounce away.



## Adhesion - Plant Interactions

*Initial* drop adhesion onto leaf surfaces is the consequence of dynamic interactions within the spray solution during flight and on impact. Hartley and Brunskill (1958) stated that small water drops, e.g. 20-50  $\mu\text{m}$  in diameter, will adhere to all plant surfaces and that large drops, ( e.g. 3000  $\mu\text{m}$  ) will fragment on impact. At 50  $\mu\text{m}$  the surface energy of the droplet far exceeds its kinetic energy, whereas at 3000  $\mu\text{m}$  the kinetic energy exceeds the surface energy by so much that it is not surprising that there is kinetic energy to disrupt the drop rather than reflect it. Anderson and Hall (1989) provided the first experimental data that identified dynamic surface tension, as opposed to equilibrium surface tension, to be linked to spray retention. Dynamic surface tension is strongly affected by surfactant structure and solution concentration ( Policello *et al.*, 1993; Wirth *et al.*, 1991 ), and these factors will contribute to leaf adhesion. Organosilicone surfactants reduce surface tension more rapidly, and to lower values than do many other surfactants, and can therefore further enhance drop adhesion ( Stevens *et al.*, 1993). Organosilicone surfactants were expected for these reasons to provide an advantage over conventional hydrocarbon-based surfactants for spray adhesion.

The microroughness of the leaf surface is a relevant retention/adhesion -determining factor. Leaf surfaces with crystalline epicuticular waxes have been shown to retain less spray solution than species characterized by a smooth cuticular surface ( Hartley and Brunskill, 1958; Anderson *et al.*, 1987; De Ruiter *et al.*, 1990; Wirth *et al.*, 1991).

This study will use *Quercus rubra* (red oak), *Acer rubrum* (red maple) and *Liquidambar styraciflua* (sweetgum) seedlings, a small sample of the many common woody weed species competing within Southern USA conifer plantations. Scanning electron microscopy (SEM) studies of the surface of leaves from red oak and red maple( Brakke *et al.*, 1993) showed large differences between species and large differences between the adaxial and abaxial surface of each species. For this reason, adhesion measurements were carried out on both the adaxial and the abaxial leaf surface of the three tree species being studied ( Objective 2). Brakke's SEM observations confirmed the greater roughness of the abaxial side of the leaf, therefore less adhesion to the abaxial surface was anticipated. Both the adaxial and abaxial leaf surfaces of red

maple are rougher than red oak leaves, which is one reason why this study looked to see if wax structure and leaf angle could explain retention ( Objective 4).

### **Spray Retention**

It is possible to have zero adhesion, but have a very high percentage retention, which indicates that there is either reflection of the parent drop or satellite droplets for a short distance, with subsequent capture on the same leaf, or that there is substantial retention of solution from the parent drop in the first instance.

The volume of spray retained by a plant depends both on the gross morphology and on the nature of the surfaces of the plant. First, the amount intercepted by the foliage will depend on the leaf area and degree of overlapping, and angle of incidence to the spray. Second, the proportion of intercepted spray droplets which is actually retained and the proportion which is shed by the leaves depends on many characteristics of the foliage. Retention may be low because the spray droplets rebound from the leaf surface on impact, or because the droplets do not adhere sufficiently to the inclined surfaces and hence roll off. Retention can also be disproportionately low at high volume rates of application because the surface is so readily wetted that the spray solution forms a continuous film and the excess runs off the leaf margins (Holly, 1976).

In low-volume spraying, run-off is unlikely since all the spray that impacts should remain on the target surface. The spray should be formulated and applied in such a way that run-off is avoided (Furmidge, 1962). On the other hand many high-volume sprays are applied to beyond run-off in order to improve target coverage. This is not the case in forest applications. However the addition of organosilicones may cause run-off. Due to the extreme spreading of organosilicones, relative to conventional surfactants (Zabkiewicz *et al.*, 1988; Murphy *et al.*, 1991) there may be limited retention, despite high initial levels of adhesion. This has been observed with sprays incorporating an organosilicone surfactant applied at high volume to an apple orchard with airblast equipment (Stevens and Zabkiewicz, 1990).

The leaf shape of individual leaves and their orientation with respect to the spray determines the amount of spray that comes into contact with the shoot ( stem, together with its leaves ) tissue. Only plant surfaces in the direct path of the spray will intercept herbicide, unless through secondary interception. Other parameters being equal, the greater the surface area of leaves oriented perpendicular to the spray, the greater will be the interception of the herbicide ( Hess,1987)

## **APPLICATION TECHNOLOGIES**

Previous studies examining the effects of carrier volume, spray droplet size and concentration, on efficacy of broadcast foliar treatments, have shown variable results. Practitioners experience conflicting goals of application design. First, there is a desire to reduce application costs by lowering the amount of carrier used per acre. Reducing spray volume decreases the time and expense required for hauling and loading high volumes of water, and allows more land area to be covered with a single tank of spray solution. However, this may result in poorer efficacy because total coverage is reduced, as is the penetration of the spray, into the lower canopy layers. Second, there is a desire to increase droplet size to reduce the potential for drift. This can also lower coverage but generally improves penetration to the lower canopy layers. Past studies have shown that smaller droplets may result in better distribution over the leaf surface, better absorption into the leaf and improved translocation into other plant tissue (Brady, 1972; Ambach and Ashford, 1982; Buehler and Burnside, 1983; Buehler and Burnside, 1987; Boerboom and Wyse, 1988; Cazell *et al.*, 1990 ).

For these reasons three different drop sizes were studied. This study considered droplets of a size produced by the microfoil boom sprayer and the radiarc sprayer, as used in forestry practices in the Southern USA, along with a droplet size more common to NZ forestry practices. The radiarc sprayer was used in the field trial carried out in Virginia.

### **Microfoil boom sprayer**

The majority of herbicide applications made to US forests are broadcast sprays applied from helicopters (Kidd, 1987). Aerial methods are preferred in the case of steep terrain or for difficult to reach area's limiting ground-based systems, and the speed and flexibility afforded in treating large acreage's. The most common system used is the microfoil boom. The microfoil boom has nozzles placed in a boom shaped like an aerofoil, which minimizes turbulence at the point where droplets are formed. Primary droplets from microfoil nozzles are about twice the size of the orifice. A low, 13.8 kilopascal, pressure at the needle-like orifices along the trailing edge of the nozzle helps reduce the shear forces which cause the fine droplets that are subject to drift. Smaller satellite droplets are formed from thin filaments of spray between the primary droplets, but proper nozzle orientation will result in the capture of small droplets by large droplets in smooth air behind each nozzle. Spray falls to the ground in a uniform sheet, rather than drifting down in a mist of droplets. Droplets of 800  $\mu\text{m}$  are produced with a microfoil boom equipped with a 0.33-mm nozzle and 1700  $\mu\text{m}$  from a 0.71-mm nozzle, with a variation of only 200  $\mu\text{m}$  (Kidd, 1987).

### **Radiarc sprayer**

The Radiarc is a controlled droplet application (CDA) system. It uses direct electrical power with rheostat adjustments to oscillate, in opposite directions, two circular heads that contain 11 tips each. It combines spray pressure ( about 40 psi, 276 kpa) and centrifugal force to produce uniform droplets of large diameter to minimize drift. The 22 tips are evenly spaced around half the circular heads, producing semi-circles of radiating spray that merge through oscillation behind and to the sides of the tractor. Spray pattern versatility is provided by a range of spray tip sizes ( diameter of orifice) that are available from the manufacturer: 0.76mm (0.030 in.), 1.14mm (0.045 in.), 1.78mm (0.070 in.), 2.16mm (0.085 in..) and 2.56mm (0.101 in.). These tip sizes as well as plugs can be placed in any of the 22 positions to regulate output. The manufacturer states that less control over precise droplet size occurs when using the 1.78mm and larger tips

( Miller,1991). The 0.76mm and 1.14mm orifice sizes are used in forest site preparation, and the 0.76mm orifice size is used for forest release sprays ( pers. com. Waldrum Specialties, Inc.). These orifice sizes produce 1500  $\mu\text{m}$  and 2250  $\mu\text{m}$  size droplets.

## **CONTACT PHYTOTOXICITY**

While foliar uptake may be sufficient to control agronomic plants, translocation is the key to woody plant control, due to the need to prevent resprouting ( Cazell *et al.*, 1990). Contact phytotoxicity is the observed damage to leaf tissue (including cell death) after spray droplet contact and is usually determined after a specified time (within the first 24 hours). In certain applications, contact phytotoxicity has been shown to isolate and confine the a.i. physiologically to the site of penetration, thereby decreasing performance (Ennis and Williamson, 1963; McKinlay *et al.*, 1972; Merritt, 1980; Geiger and Bestman, 1990). Some investigators have reported that small droplets are more potent than large ones because they cover more evenly, injure the target areas less, and allow the a.i. to penetrate and translocate better (Douglas, 1968; Ennis and Williamson, 1963; Lake, 1977; McKinlay *et al.*, 1974; Mckinlay *et al.*, 1972; Merritt, 1982; Merritt and Taylor, 1977; Prasad and Cadogan 1992; Prasad, 1985; Wilson and Taylor, 1978 ). Others however, report that large drops are more effective than small drops (Smith, 1946). Still others (Ayres *et al.*, 1982; Bode, 1984; Gebhardt *et al.*, 1986; Maybank, 1981; Mullison, 1953) found that droplet size did not influence weed control under field conditions.

## **SUMMARY**

To summarize, the most important points covered in the literature review that need to be considered in order to enhance triclopyr amine efficacy are: contact phytotoxicity which needs to be minimized so that translocation is not hindered, droplet size and concentration of active may be important factors in terms of contact phytotoxicity; the addition of an organosilicone surfactant should increase both the initial adhesion of a droplet and the overall retention of the spray solution, compared to the formulation containing active alone, or active plus conventional surfactants; droplet size may be an important factor with respect to initial adhesion and overall

retention; the addition of an organosilicone surfactant should increase the spread area of the spray on the leaf surface, possibly to the extent of obtaining a “wrap-around” effect to the surface of the leaf not directly exposed to the spray; there will probably be differences in initial adhesion and overall retention between the adaxial and abaxial leaf surface of each tree species being studied, and among the tree species being studied, due to the differences in microroughness of the leaf surfaces.