Alam Sundaram

# INFLUENCE OF TWO POLYMERIC ADJUVANTS ON PHYSICAL PROPERTIES, DROPLET SPREADING AND DRYING RATES, AND FOLIAR UPTAKE AND TRANSLOCATION OF GLYPHOSATE IN VISION® FORMULATION.

---

REFERENCE: Sundaram, A., "Influence of Two Polymeric Adjuvants on Physical Properties, Droplet Spreading and Drying Rates, and Foliar Uptake and Translocation of Glyphosate in Vision® Formulation", Pesticide Formulations and Application Systems: 10th Volume, ASTM STP 1078, L.E. Bode, J.L. Hazen and D.G. Chasin, Eds., American Society for Testing and Materials, Philadelphia, 1990.

ABSTRACT: The effect of Sta-Put® and Silwet® L-7607 on physical properties (viscosity, surface tension and volatility), droplet spreading and drying rates, and foliar uptake and translocation of glyphosate was studied using white birch seedlings and branch tips. Three end-use mixtures were prepared using Vision®, one in water alone and the other two with 0.05% of the adjuvants in water. Physical properties were measured to examine their roles on droplet spreading and drying rates. Foliar uptake was investigated to study the effect of droplet spreading and drying rates on foliar retention; and translocation was studied to examine the role of the two polymers on bioavailability of glyphosate.

The adjuvants did not contribute to marked differences in the viscosities or volatilities of the three end-use mixtures, although the surface tensions were altered to some extent. Silwet caused a marked increase in the droplet spread areas, along with a simultaneous decrease in the droplet drying time. Sta-Put did not alter any of these parameters. No simple relationship could be found between surface tensions of the mixtures and droplet spreading or drying rates. Both adjuvants contributed to an increase in the foliar uptake of glyphosate, but Silwet caused a much greater increase than Sta-Put, thus suggesting a relationship between droplet spreading and foliar uptake. Nevertheless, there was no significant difference in the amount of glyphosate translocated between the three end-use mixtures, thus indicating no evidence of reduced bioavailability because of the presence of the two polymers at the concentration levels used in the study.

Dr. Alam Sundaram is a Research Scientist and Project Leader for Pesticide Formulations Project, at Forestry Canada, Forest Pest Management Institute, 1219 Queen Street East, P.O. Box 490, Sault Ste. Marie, Ontario, Canada P6A 5M7.

KEYWORDS: Glyphosate, herbicide end-use mixtures, polymeric adjuvants, physical properties, droplet spreading, droplet drying, foliar uptake, herbicide translocation

Polymers are used in herbicide formulations to provide beneficial effects, such as, alteration of droplet size spectra for increasing deposits on target sites [1-3], and for reducing off-target drift [4-8]. However, certain polymers can provide adverse side effects, viz., reduce herbicidal activity via entrapment of the herbicide molecules into the polymeric structure [9]. Polymers have also increased droplet spreading on foliage, provided a greater area of contact and enhanced the rate of uptake [10]. On the other hand, polymers can also accelerate droplet drying rates on foliage [11] and reduce uptake, since the loss of a liquid phase on foliage has been known to reduce cuticular penetration [12].

Sta-Put® is a polymeric adjuvant (Nalco Chemical Co., Illinois, USA) that can alter the droplet size spectra of the spray cloud indicating its potential as a "drift retardant" adjuvant [13] for herbicide tank mixes. Silwet® L-7607 is a non-ionic organosilicone copolymer surfactant (Union Carbide, Montreal, Canada) which can increase droplet spreading on foliage by reducing the contact angle [10,11]. However, data are sparse in the literature on the ability of these polymers to reduce the bioavailability of herbicides, and to alter the physical properties (viscosity, surface tension and volatility) [14] of the end-use mixes, thereby affecting droplet spreading/drying rates, foliar uptake and translocation.

The purpose of the present study was to investigate the effect of Sta-Put and Silwet polymers on physical properties, droplet spreading and drying rates, foliar uptake and translocation of glyphosate [N-(phosphonomethyl)glycine, Monsanto Agricultural Products Company, St. Louis, Missouri, USA] in the end-use mixtures of Vision® formulation [a formulation concentrate of glyphosate containing 356 g of active ingredient (AI) per liter], using white birch, *Betula papyrifera* (Marsh.) seedlings and branch tips.

## EXPERIMENTAL METHODS

### End-use Mixtures

Glyphosate end-use mixtures and other materials used in the study are listed in Table 1, along with the percentage compositions of the ingredients used in preparing them.

### Physical Properties

Physical properties measured were viscosity, surface tension and volatility. Viscosity was measured relative to water (relative viscosity) using Ostwald viscometer [15]. Surface tension and volatility were measured as described by Sundaram and Leung [16]. Volatility parameters are expressed in rate of evaporation, R(Evap), half-life (i.e., $T_{\frac{1}{2}}$, the time required for the volatile components to reach 50% of their initial concentrations), and the percent non-volatile componets (NVC%,

Table 1 - Percentage compositions of ingredients used in the glyphosate end-use mixtures

| Formulation ingredients | Percentage composition (v/v) | |
|---|---|---|
| | Mixture VW | Mixture VWSt-0.05 [a] or VWSi-0.05 [a] |
| Distilled water: | 54.19 | 54.14 |
| Vision® formulation: | 14.04 [b] | 14.04 |
| $^{14}$C-glyphosate: [c] | 31.77 | 31.77 |
| Adjuvant: | --- | 0.05 |

*a:* The formulation VWSt-0.05 contained the Sta-Put adjuvant whereas the VWSi-0.05 formulation contained the Silwet L-7607 adjuvant.

*b:* At a concentration level of 14.04 ml of Vision in 100 ml of the end-use mixture the dosage rate is equivalent to 0.5 kg of active ingredient in 10 liter per ha.

*c:* The radiolabeled product had a specific activity of 49 µCi per mg of glyphosate in 13.7 ml of solution. It contained the same isopropylamine salt of glyphosate as in Vision, along with the same surfactant in the same weight ratio.

the residual amounts which were left unevaporated until at least 120 h). All measurements were carried out at room temperature (20 ± 2°C). The data are given in Table 2.

Droplet Spreading and Drying Rates

To investigate droplet spreading and drying rates, aliquots of the three mixtures, VW, VWSt-0.05 and VWSi-0.05 (see Table 1 for the description of these mixtures), were mixed with a water-soluble fluorescent dye (Erio Acid Red, St. Lawrence Aniline Company, Brockville, Ont., Canada), at 0.2 g per 100 ml. This was intended to facilitate ready visualization of the droplet under a microscope on different surfaces. The addition of this minute quantity of the dye was tested in a previous experiment, and was found not to alter the physical properties of the three mixtures under investigation.

a. Equilibrium Spread Areas and the Associated Rates

White birch seedlings (6 month old, height 44 ± 7 cm or 66 ± 7 cm with the pot), raised from seed under greenhouse conditions, were selected for the study. The average number of leaves per seedling was 14 ± 3. Prior to the start of the study, the seedlings were allowed to acclimatize for one week in the treatment area, a part of the greenhouse maintained at a temperature of 20 ± 2°C, relative humidity of 75 ± 5%, and a photoperiod of 16 h light and 8 h darkness. The average surface area

Table 2 - Physical properties of the three end-use mixtures used in the study at 20 ± 2°C and 75 ± 5% relative humidity

| Physical properties | End-use mixtures used | | |
|---|---|---|---|
| | VW | VWSt-0.05 | VWSi-0.05 |
| Relative viscosity | 1.38 | 1.68 | 3.63 |
| Surface tension (mN/m) | 31.5 | 37.2 | 27.5 |
| Volatility data: | | | |
| i. R(Evap) [a] | 3.95 | 3.23 | 3.09 |
| ii. $T_{\frac{1}{2}}$ (min) [b] | 11.0 | 13.1 | 13.4 |
| iii. NVC% [c] | 13.0 | 15.3 | 16.9 |

*a:* Percentage weight decrease of the liquid film per min, as calculated during the initial 10 min of evaporation.

*b:* Half-life, $T_{\frac{1}{2}}$, refers to the time required for the volatile components of the mixtures to evaporate down to 50% of their initial values.

*c:* The residual amounts which were left unevaporated until at least 120 h after the start of the experiment.

of the leaves at the mid-crown level was 100 ± 5 $cm^2$ per leaf at the time of the study.

Droplets of 0 5 µl in volume (or 1000 µm in diameter) were produced using a precision micro-applicator (Instrumentation Specialties Company, 4700 Superior Lincoln, NB 68504, USA). These were collected on the adaxial surface of a mid-crown leaf at the rate of 8 droplets per 6 $cm^2$. The droplets were observed under a microscope using dim illumination to avoid undue heating of the droplet (which would increase the rate of evaporation); and the degree of spreading was examined. When the diameter of the spread area attained a constant value (the equilibrium state of spreading), the diameter was measured, and the time to reach the equilibrium state was noted. These procedures were replicated several times (minimum number of leaves used for each mixture was 10, equivalent to 80 droplets; maximum was 20 or 160 droplets), and the mean ± SD values of the spread areas were calculated for the three mixtures described in Table 1. In addition, two artificial surfaces, glass plate and an acetate transparency sheet (each 2.5 cm x 2.5 cm) (the transparency sheet was obtained from General Photography Ltd., 1350 Birchmont Road, Scarborough, Ontario, Canada) were used for the sake of comparison. The spread factor data (SF) were calculated using the equation:

$$SF = \frac{\text{Diameter of the spread area on a surface}}{\text{Diameter of the spherical droplet that would be airborne}}$$

The data on SF values and the time required for equilibrium spreading are given in Table 3.

Table 3 - Spread factor data for the three end-use mixtures on different surfaces and the time required for complete spreading of droplet[a] - temperature 20 ± 2°C and rel. humidity 75 ± 5%

| Surface type | End-use mixtures used | | |
|---|---|---|---|
| | VW | VWSt-0.05 | VWSi-0.05 |
| | Spread factor values[b] | | |
| 1. Birch leaf | 2.03 (± 0.13) | 2.02 (± 0.11) | 4.55 (± 0.13) |
| Relative spread area (RSA)[c] | 1 | 1 | 4.93 |
| 2. Glass plate | 2.63 (± 0.11) | 2.42 (± 0.09) | 5.20 (± 0.14) |
| Relative spread area (RSA)[c] | 1 | 1 | 4.33 |
| 3. Acetate sheet | 1.54 (± 0.04) | 1.54 (± 0.03) | 3.60 (± 0.04) |
| Relative spread area (RSA)[c] | 1 | 1 | 5.46 |
| | Time (min) required for complete spreading[b] | | |
| 1. Birch leaf | 15.3 (± 0.60) | 16.9 (± 0.70) | 8.00 (± 0.65) |
| 2. Glass plate | 7.03 (± 0.45) | 9.07 (± 0.53) | 4.59 (± 0.37) |
| 3. Acetate sheet | 10.2 (± 0.45) | 12.0 (± 0.53) | 7.05 (± 0.37) |

*a:* The size of the droplet used was 0.5 µl in volume or 1000 µm in diameter.

*b:* The data represent the mean ± SD of at least 80 replicate droplet measurements.

*c:* Calculated as:

$$RSA = \frac{\pi/4\ (\text{diam. of spread area for VW with adjuvant})^2}{\pi/4\ (\text{diam. of spread area for VW without adjuvant})^2}$$

In some instances, the spread area of the droplet failed to form a circular stain on the foliar surface. In these cases, the total area of the stain was determined microscopically, and the diameter of the circle that would have the same area as the non-circular stain on foliage was calculated for computing the spread factor.

b. Droplet Drying Rates

For droplet drying rates, a method was developed based on the principle that liquids can be sheared by application of pressure much more easily than solids. If a liquid droplet was collected on a leaf surface the droplet would spread, evaporate and penetrate into leaf cuticle at the same time. If the initial ingredients of the droplet were non-volatile and volatile liquids, the evaporated droplet would leave a liquid residue of diameter D1 on the leaf surface. Upon application of pressure, the diameter of the droplet would noticeably increase to D2. In contrast, if the initial ingredients were solids and volatile liquids, the evaporated droplet would leave a solid residue (with a diameter D1), but when pressure was applied the diameter would not increase noticeably. These principles were used to develop a method for determining the time required for complete drying of droplets on surfaces.

Droplets of 0.5 µl in volume were generated as described above, and were collected on a 6-$cm^2$ area of a mid-crown birch leaf. The drying process was observed with respect to time, visually during the initial stages, i.e., until the shiny appearance (due to reflection of light) of the droplet surface had lasted. The droplets were then left to dry for another 2 min, and the diameter (D1) of the spread area was measured microscopically. The time lapse (T1), i.e., from the time of droplet collection on the leaf until diameter measurement, was noted. Since this stage may not represent a completely evaporated droplet, further testing for droplet dryness was carried out by placing a clean acetate sheet (6 $cm^2$ area) over the birch leaf. A force of 100 g-weight was applied gently onto the top acetate sheet without causing any lateral movement of the assembly. After 2 min, the weight was removed and the assembly was placed under a microscope for diameter (D2) measurement of the droplet spread area. If D2 was the same as D1, then the droplets were completely dry and consisted of a solid phase, and the time T1 was taken as that required for complete drying of the droplet. If D2 was greater than D1, this indicated a liquid droplet (either a partially evaporated droplet or a droplet consisting of a non-volatile liquid phase). Therefore, the experiment was repeated using a fresh birch leaf. This time, the drying process was observed for a period (T2) which was 15 min longer than T1 (i.e., T2 = T1 + 15), and the entire process was carried out. After a lapse of T2 min, the diameter D3 was measured and another acetate sheet was placed, followed by the 100 g-weight. Two min later the diameter D4 was measured. If D4 was equal to D3, then the droplets were dry, and the time T2 was taken as required for complete drying of droplets. This procedure was repeated 'n' times until Dn became equal to $D_n$-1. The time that was needed to attain the constant $D_n$-1 value was taken as that required for the complete (or maximal) drying of the droplet. Following this procedure, the droplet drying times were determined for the three end-use mixtures listed in Table 1, and the data are given in Table 4.

In addition to the birch leaf, glass plate and acetate sheet surfaces were also used for the investigation in the same manner (Table 4).

Table 4 - Time required for droplet[a] drying on birch leaf, glass plate and acetate sheet for the three end-use mixtures used in the study - temperature 20°C, rel. humidity 75 ± 5%

| Surface type | End-use mixtures studied | | |
|---|---|---|---|
| | VW | VWSt-0.05 | VWSi-0.05 |
| Birch leaf | > 360[b] | > 360 | 240 |
| Glass plate | > 360 | > 360 | 180 |
| Acetate sheet | > 360 | > 360 | 180 |

*a:* The size of the spherical droplet was 1000 µm in diameter.

*b:* The data represent the mean of at least 10 replicates.

## Foliar Uptake and Translocation

Foliar uptake and translocation were investigated using two types of studies, viz., using 6-month old birch seedlings and branch tips cut out from the 6-month old seedlings.

a. Study I - Using Birch Seedlings

Twenty-six seedlings (description same as that under "Equilibrium Spread Areas and the Associated Rates") were selected for Study I. The seedlings were divided into four groups, A, B, C and D. Groups A to C consisted of 8 seedlings each, and group D, of 2 seedlings. Group A received the VW mixture; group B, VWSt-0.05; and group C, VWSi-0.05. Group D served as the control, for measuring the background radioactivity in the plants.

A 40 µl volume (containing 101000 disintegration per min [dpm] of radioactivity) of the three end-use mixtures (Table 1) was applied to each seedling in 80 x 0.5 µl droplets (each 1000 µm in diameter) to the adaxial surface of four mid-crown leaves, at the rate of 20 droplets per leaf (or 0.2 droplet per $cm^2$), using the micro-applicator described earlier. This dosage regime provided an application rate of 0.5 kg AI in 10 liter per ha area of the treated leaves.

Out of the eight seedlings used for each formulation, two were harvested at each of the four post-treatment periods, i.e., 8, 24, 48 and 72 h respectively. Each plant was divided into four segments, viz., leaves above treated leaves, stem, leaves below treated leaves and root. The adaxial surface of the treated leaves were individually rinsed with 2 x 20 ml of distilled water into a graduated cylinder (the time duration for each rinsing was 30 s). This procedure was repeated for the

other three treated leaves and the total rinsings were pooled. Exactly 3 ml volume of the rinse solution (described as the treated-leaf wash) was transferred into a scintillation vial containing 17 ml of a liquid scintillant (Scinti Verse™ II, SO-X-12, Fisher Scientific Company, New Jersey, USA) for $^{14}C$-assay. All plant parts [including the washed treated leaves (described as the treated-leaf residue)] were then oven-dried for 4 h at 60°C, weighed and combusted in a biological oxidizer (Packard Oxidizer, Model 306, United Technologies Packard, Packard Instrument Company, Illinois, USA). The evolved $^{14}CO_2$ was absorbed in vials containing Carbosorb® (an aqueous scintillant for absorbing $^{14}CO_2$, United Technologies Packard, Illinois, USA) for $^{14}C$-assay.

The soil in the pot was not assayed for radioactivity because in a previous study soil samples showed little $^{14}C$-content, indicating negligible exudation of glyphosate via root (unpublished data). The radioactivity of all plant samples and leaf extracts was determined by a Beckman LS9000 liquid scintillation counter with a built-in automatic external standardization to determine counting efficiency. The range of counting efficiency was 93 to 97%, and the data in Table 5 were corrected for these factors. Because few glyphosate metabolites have been reported in plants within 72 h after treatment [17,18] the radioactivity recovered will be referred to as $^{14}C$-glyphosate.

b. Study II - Using Birch Branch Tips

Because only two seedlings were used at each sampling time for each end-use mixture, only a preliminary estimate of $^{14}C$-distribution in plant sections can be made at different time intervals (Table 5). To obtain more meaningful information on differences in foliar uptake and bioavailability between the three end-use mixtures, several seedlings would be required per mixture. However, the use of a large number of seedlings would involve extensive labour, time and cost of the materials. To overcome this problem, small branch tips were used in Study II.

Twenty-six branch tips (each 20 cm long containing three fully developed young leaves) were clipped from the top portion of the 6-month old seedlings (one branch tip from each seedling). The under-developed young leaves, except the shoots, were removed and discarded, leaving only the three fully-developed leaves and shoots in the branch tip. The stem of each branch was placed at once in a 50 ml capacity plastic vial containing tap water, and the branch was supported upright by a tubing and a lid with a hole. Similar branch clippings were tested for their survival rate and growth patterns for a period up to 72 h in a preliminary investigation prior to the actual study; and it was observed that the branches remained quite healthy and showed small but significant amount of weight gain during this period.

Twenty-four branches were equally divided into 3 groups, G, H and J. Group G received VW mixture, group H, VWSt-0.05 and group J, VWSi-0.05. The remaining two branches (group K) served as the control for measuring the background radioactivity in the plants. A 10-µl volume (containing 25250 dpm of radioactivity) of the mixture was applied to one leaf (surface area 100 $cm^2$). For relevant details see under 'Study I'.

The eight branches used for each formulation were harvested at 48 h post-treatment. This time period was considered as adequate for detecting

Table 5. Foliar uptake and translocation of glyphosate into different parts of white birch seedlings following treatment with three end-use mixtures

| Sample description | End-use mixtures | Percentage distribution * | | | |
|---|---|---|---|---|---|
| | | 8h | 24h | 48h | 72h |
| Treated leaves | VW | 24.6 ± 5.0 | 38.6 ± 6.5 | 42.4 ± 1.4 | 43.8 ± 3.8 |
| | VWSt-0.05 | 35.7 ± 0.2 | 44.5 ± 6.5 | 46.2 ± 3.3 | 57.1 ± 15.2 |
| | VWSi-0.05 | 38.9 ± 1.3 | 49.7 ± 3.5 | 52.5 ± 4.4 | 63.5 ± 10.2 |
| Leaves above treated leaves | VW | 0.1 ± 0.02 | 0.5 ± 0.02 | 1.1 ± 0.7 | 0.9 ± 0.1 |
| | VWSt-0.05 | 0.2 ± 0.01 | 0.4 ± 0.10 | 0.6 ± 0.4 | 0.8 ± 0.6 |
| | VWSi-0.05 | 0.2 ± 0.05 | 0.5 ± 0.10 | 0.7 ± 0.3 | 1.0 ± 0.6 |
| Leaves below treated leaves | VW | 0.1 ± 0.03 | 0.2 ± 0.01 | 0.2 ± 0.02 | 0.4 ± 0.20 |
| | VWSt-0.05 | 0.3 ± 0.20 | 0.3 ± 0.10 | 0.2 ± 0.03 | 0.2 ± 0.01 |
| | VWSi-0.05 | 0.3 ± 0.10 | 0.3 ± 0.10 | 0.3 ± 0.05 | 0.3 ± 0.10 |
| Stem | VW | 2.9 ± 0.9 | 7.6 ± 1.8 | 8.9 ± 3.1 | 12.1 ± 0.6 |
| | VWSt-0.05 | 2.5 ± 0.5 | 7.3 ± 1.1 | 9.1 ± 2.8 | 8.5 ± 1.0 |
| | VWSi-0.05 | 2.8 ± 0.6 | 7.1 ± 1.0 | 8.9 ± 1.9 | 10.5 ± 0.9 |
| Root | VW | 2.4 ± 0.4 | 4.4 ± 2.6 | 5.6 ± 0.7 | 8.0 ± 2.0 |
| | VWSt-0.05 | 2.8 ± 1.3 | 6.7 ± 2.6 | 10.5 ± 0.8 | 11.2 ± 3.0 |
| | VWSi-0.05 | 3.2 ± 1.2 | 7.7 ± 1.5 | 11.5 ± 0.9 | 13.9 3.3 |
| Plant total | VW | 30.1 | 51.3 | 58.2 | 65.2 |
| | VWSt-0.05 | 41.5 | 59.3 | 66.6 | 77.8 |
| | VWSi-0.05 | 45.4 | 65.3 | 73.9 | 89.2 |
| Leaf wash | VW | 69.9 ± 3.8 | 48.7 ± 10.8 | 41.8 ± 4.4 | 34.8 ± 2.5 |
| | VWSt-0.05 | 58.5 ± 1.7 | 40.7 ± 5.7 | 33.4 ± 7.3 | 22.2 ± 6.8 |
| | VWSi-0.05 | 54.6 ± 2.0 | 34.7 ± 4.7 | 26.1 ± 5.7 | 10.8 ± 3.3 |

* Values represent the mean of two sets of data obtained from the trees.
All values were corrected for the $^{14}C$-counting efficiency.
Percentage distribution values were calculated as:

$$\% \text{ Distribution} = \frac{\text{Radioactivity recovered in sample}}{\text{Total radioactivity recovered}} \times 100$$

Table 6. Foliar uptake and translocation of glyphosate into birch branch tips at 48 h after treatment with three end-use mixtures

| Sample description | Percentage distribution of radioactivity* for mixtures | | |
|---|---|---|---|
| | VW | VWSt-0.05 | VWSi-0.05 |
| Treated leaf | 39.9 ± 2.62 $^{a}$ | 44.1 ± 2.88 $^{b}$ | 52.1 ± 2.94 $^{c}$ |
| Remaining parts | 1.31 ± 0.42 $^{d}$ | 1.65 ± 0.58 $^{dg}$ | 2.01 ± 0.2 $^{g}$ |
| Leaf wash | 58.8 ± 2.66 $^{h}$ | 54.2 ± 2.45 $^{j}$ | 45.9 ± 2.86 $^{k}$ |
| Tap water in vial | --- | --- | --- |

* Values represent the mean ± SD obtained from eight sets of data obtained from eight branch tips used for each end-use mixture.

All values were corrected for the $^{14}C$-counting efficiency.

Percentage distribution values were calculated as:

$$\% \text{ Distribution} = \frac{\text{Radioactivity recovered in sample}}{\text{Total radioactivity recovered}} \times 100$$

$^{a-k}$Values with the same superscript letters are not significantly different from one another (Student-Newnam-Keuls test, error rate $\alpha > 0.05$).

this lies in the very high values of droplet spread areas observed for VWSi-0.05. The higher the droplet spreading, the faster the evaporation of volatile components, and therefore, less amount of time would be required for complete spreading of the droplet. In summary, the present data emphasize the complexity of the interactions between surface tension, volatility and the physicochemical nature of the collection surfaces on the spreading capability of the different liquids.

Influence of Physical Properties of the End-use Mixtures on Droplet Drying Times

The data in Table 4 indicate markedly lower drying times for the droplets of VWSi-0.05 than for VW or VWSt-0.05. Regardless of the nature of the surfaces used, VWSi-0.05 dried the fastest, i.e., in about 3 to 4 h after treatment, whereas, VW and VWSt-0.05 did not show complete drying even after 6 h. The reason for this behavior was the formation of a thick waxy crust over the droplets of VW or VWSt-0.05 (this layer was visible when viewed under a microscope). This layer must have slowed down the rate of evaporation of water molecules escaping into the ambient air. Consequently, the inner core of the droplet remained as liquid, and the droplets failed to dry completely even after 6 h. Such a crusty layer was not visible in the case of VWSi-0.05, probably because of excessive spreading, and that is perhaps why the droplets were dried out completely in 3 to 4 h after treatment.

Foliar Uptake and Translocation of Glyphosate

a. Study I - Using Birch Seedlings

The data in Table 5 indicate that foliar uptake of glyphosate is relatively a slow process since more than 50% was washed off into the leaf rinse at 8 h after treatment, irrespective of the end-use mixture tested. However, as the exposure duration increased, the uptake gradually increased to 44 to 64% depending on the adjuvant, and only about 10 to 35% was washed off at 72 h.

Similar to the foliar uptake, the translocation of glyphosate from the treated leaf into other parts of the plants is also shown to be slow because only about 6% of the applied amount was translocated at 8 h after treatment, and about 94% remained in the treated leaf. However, with the increased exposure, translocation increased gradually and reached 21 to 25% at 72 h (Table 5). Nevertheless, the treated leaf still contained about 75 to 79% of the applied amount, thus indicating incomplete translocation even after 72 h. The amount of radioactivity detected in the stem and root sections increased gradually from the 8 h value to about 4 to 5 times higher at 72 h. The present findings are in agreement with those reported in the literature [21], although the amount absorbed and translocated was higher in the present study than in those reported.

Regarding the influence of the two polymeric adjuvants on the bioavailability of glyphosate, the present data indicate no evidence of glyphosate entrapment into the polymeric chain, thereby making it less

bioavailable. On the contrary, the two adjuvants contributed to a significant increase in foliar uptake, as indicated by analysis of variance test (ANOVA $P \leq 0.05$), but yet the translocated amount seemed to be similar for all three end-use mixtures (Table 5).

b. Study II - Using Birch Branch Tips

The results obtained from the eight branch tips used in Study II for each mixture were subjected to statistical treatment using the Studen-Newman Keuls test (S-N-K) [22]. The data indicated that on average, ca. 60% of the applied amount was washed off at 48 h from the leaf treated with VW, as opposed to 54% with VWSt-0.05 and 46% with VWSi-0.05 (Table 6), thus indicating a significant increase (S-N-K test, error rate $\alpha \leq 0.05$) in the 'apparent foliar uptake' because of the presence of the two adjuvants. The amount translocated into the remaining parts of the branch tip was low and ranged from 1.3% (for VW) to 2.0% (for VWSi-0.05). No significant difference was noted in the translocated amount between VW and VWSt-0.05, or between VWSt-0.05 and VWSi-0.05; but a significantly higher amount was translocated due to the presence of the Silwet adjuvant in VWSi-0.05, compared to the VW mixture.

Little radioactivity was detected in the tap water in vial, thus indicating negligible movement of glyphosate *via* stem into water.

The significant increase in the 'apparent foliar uptake' of glyphosate arising from the presence of the Sta-Put and Silwet polymers, does not necessarily indicate an increase in penetration of glyphosate through the leaf cuticle, since the adjuvants could have simply provided a protective layer over the droplets, thus reducing the amount being washed off during rinsing. Without detailed investigations using extracted plant cuticle [23], it would not be possible to conclude whether the two polymers actually increased the foliar uptake of glyphosate, or simply provided a protective film over the droplets. Nevertheless, the present study indicated no evidence of reduced bioavailability of glyphosate *via* adsorption or entrapment into the polymeric structure of Sta-Put or Silwet L-7607 at the concentration levels used in the study.

Influence of Droplet Spreading and Drying on Foliar Uptake and Translocation of Glyphosate

The droplet spreading patterns and drying times were very similar for VW and VWSt-0.05, indicating that the Sta-Put adjuvant did not contribute to any changes in these parameters. However, the adjuvants caused a significant increase (by ca. 4%) in the apparent foliar uptake. In contrast, Silwet L-7607 contributed to a marked increase in droplet spreading compared to Sta-Put, and therefore is expected to enhance foliar uptake markedly. The observed data are in agreement with this, since the 'apparent foliar uptake' was 8% higher for VWSi-0.05 than for VWSt-0.05, and 12% higher than for VW alone (Table 6). The present study suggests the possible advantages of adding Silwet L-7607 adjuvant to herbicide mixtures, because it enhanced droplet spreading on target foliage, decreased the amount of glyphosate being wa ed off, and increased foliar retention, although the chemical nature of Silwet L-7607 could have contributed to the higher foliar uptake. Without detailed investigations on foliar uptake using several Silwet® adjuvants which would cause different degrees of droplet spreading, it is not possible

to conclude that enhanced droplet spreading would likely increase foliar uptake of herbicides.

The fact that the droplet of VWSi-0.05 dried sooner than those of VW or VWSt-0.05 did not seem to affect foliar uptake and translocation (Tables 4 and 6), an observation in contrast with that reported [12]. The reason for this deviation is not clear and requires further investigations.

## ACKNOWLEDGEMENTS

The author wishes to acknowledge with thanks the help of Mr. Donald Buckley in providing the white birch seedlings; and Messers J.W. Leung, J.K. Hatherley and J. Studens for their technical assistance in carrying out the numerous measurements required for this investigation.

## REFERENCES

[1] Sundaram, A., Leung, J.W. and Curry, R.D., "Influence of Adjuvants on Physicochemical Properties, Droplet Size Spectra and Deposit Patterns: Relevance in Pesticide Applications", Journal of Environmental Science and Health, Vol. B22, No. 3, May/June 1987, pp. 319-346.

[2] Sparks, B.D., Sundaram, A., Kotlyar, L., Leung, J.W. and Curry, R.D., "Physicochemical Properties, Atomization and Deposition Patterns of Some Newtonian Spray Mixtures of Glyphosate Containing Two Spray Modifier Adjuvants", Journal of Environmental Science and Health, Vol. B23, No. 3, May/June, 1988, pp. 235-266.

[3] Goering, C.E. and Butler, B.J., "Paired Field Studies of Herbicide Drift", Transactions of the ASAE, Vol. 18, 1975, pp. 27-34.

[4] McNulty, J.J., Anderson, G.W. and Stephenson, G.R., "Evaluation of Low Pressure Nozzles and Nalco-Trol for Reducing Drift with 2,4-D", Canadian Weed Council Research Reports, 1977, p. 316.

[5] Stephenson, G.R., Ellise, P., Desai, P.D. and Curtis, L.R., "Evaluation of Nalco-Trol for Reducing Herbicide Drift in Roadside Spraying", Abstracts, Weed Science Society of America, Vol. 116, 1977, p. 59.

[6] Yates, W.E., Akesson, N.B. and Bayer, D., "Effects of Spray Adjuvants on Drift Hazards", Transactions of the ASAE, Vol. 19, 1976, pp. 41-46.

[7] Yates, W.E., Cowden, R.E. and Akesson, N.B., "Effects of Nalco-Trol on Atomization", USDA Forest Service, Forest Pest Management Report, FPM-85-2, Davis, California, 1985, 37 pp.

[8] Richardson, R.G., "Control of Spray Drift with Thickening Agents", Journal of Agricultural Engineering Research, Vol. 19, pp. 227-231.

[9] Doub, J.P., Wilson, H.P. and Hatzios, K.K., "Comparative Efficacy of Two Formulations of Alachlor and Metalachlor", Weed Science, Vol. 36, pp. 221-226.

[10] Zabkiewicz, J.A., Gaskin, R.E. and Balneaves, J.M., "Effect of Additives on Foliar Wetting and Uptake of Glyphosate into Gorse (Ulex europaeus), in Application and Biology, BCPC Monograph No. 28, E.S.E. Southcombe, Ed., Proceedings of a Symposium,

British Crop Protection Council, Croydon, England, 1985, pp. 127-134.

[11] Zabkiewicz, J.A., Coupland, D. and Ede, F., "Effects of Surfactants on Droplet Spreading and Drying Rates in Relation to Foliar Uptake", in Pesticide Formulations: Innovations and Development, American Chemical Society Symposium Series, Vol. 371, American Chemical Society Publications, Washington, D.C., 1988, pp. 77-89.

[12] Hess, F.D., "Herbicide Absorption and Translocation and Their Relationship to Plant Tolerance", in Weed Physiology, Vol. II, Herbicide Physiology, S.O. Duke, Ed., CRC Press, Inc., Boca Raton, Florida, 1984, pp. 191-215.

[13] Bouse, L.F., Carlton, J.B. and Jank, P.C., "Use of Polymers for Control of Spray Droplet Size", American Society of Agricultural Engineers, Paper No. AA-86-005, St. Joseph, Michigan, USA, 1986, 18 pp.

[14] Sundaram, A., "Drop Size Spectra, Spreading and Adhesion; and Physical Properties of Eight Bacillus thuringiensis Formulations Following Spray Application Under Laboratory Conditions", in 9th Symposium on Pesticide Formulations and Application Systems "International Aspects", ASTM STP 1036, J.L. Hazen and D.A. Hovde, Eds., American Society for Testing and Materials, Philadelphia, 1989, pp. 129-141.

[15] Glasstone, S., Textbook of Physical Chemistry, 2nd edition, Macmillan and Co., London, England, 1955, p. 498.

[16] Sundaram, A. and Leung, J.W., "A Simple Method to Determine Relative Volatilities of Aqueous Formulations of Pesticides", Journal of Environmental Science and Health, Vol. B21, No. 2, March/April, 1986, pp. 165-190.

[17] Devine, M.D. and Bandeen, J.D., Fate of Glyphosate in Agropyron repens (L.) Beauv. Growing Under Low Temperatures", Weed Research, Vol. 23, 1983, pp. 69-75.

[18] Zandstra, B.H. and Nishimoto, R.K., "Movement and Activity of Glyphosate in Purple Nutsedge", Weed Science, Vol. 25, 1977. pp. 268-274.

[19] Neustadter, E.L. "Surfactants in Enhanced Oil Recovery", in Surfactants, Th. F. Tadros, Ed., Academic Press, Inc., London, England, 1984, pp. 277-285.

[20] Sands, R. and Bachelard, E.P., "Uptake of Picloram by Eucalypt Leaf Discs", New Phytol., Vol. 72, 1973, pp. 69-86.

[21] Masiunas, J.B. and Weller, S.C., "Glyphosate Activity in Potato (Solanum tuberosum) Under Different Temperature Regimes and Light Levels", Weed Science, Vol. 36, 1988, pp. 137-140.

[22] Steel, R.G.D. and Torrie, J.H., Principles and Procedures of Statistics: A Biometrical Approach, 2nd edn., McGraw-Hill Book Company, New York, 1980, pp. 172-194.

[23] Baker, E.A., Hunt, G.M. and Stevens, P.J.G., "Studies of Plant Cuticle and Spray Droplet Interactions: A Fresh Approach", Pesticide Science, Vol. 14, 1983, pp. 645-658.