Foliar Penetration and Dissipation of Triclopyr Butoxyethyl Ester Herbicide on Leaves and Glass Slides in the Light and Dark

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The disposition of triclopyr BEE [butoxyethyl ester of [(3,5,6-trichloro-2-pyridinyl)oxy]acetic acid] from spray mix droplets on excised Pacific madrone (*Arbutus menziesii* Pursh.) and giant chinkapin [*Castanopsis chrysophylla* (Dougl.) A. DC.] leaves and glass microscope slides was determined in a factorial laboratory experiment. Factors were temperature (10, 25, and 40 °C), illumination (light or dark), and time (from 0 to about 4100 min in 820-min increments). Triclopyr BEE penetration into chinkapin leaves is greater than into madrone leaves at all temperatures. Foliar penetration into madrone leaves did not increase between 25 and 40 °C. Losses in the dark were greatest from glass slides and least from chinkapin. Triclopyr BEE loss from chinkapin leaves at 40 °C in the light was equivalent to loss in the dark at 40 °C. Losses of triclopyr BEE from both glass slides and madrone leaves were greater in the light treatments. Models were developed by using mass balance coefficients. Results from outdoor exposures fell within 95% confidence intervals of model predictions of triclopyr BEE fate.

INTRODUCTION

The purpose of this study was to determine the short-term dissipation of triclopyr butoxyethyl ester in deposits of an aqueous tank mix of Garlon 4 formulation on glass microscope slides and foliage of two evergreen broadleaf weeds in Pacific Northwest forests as influenced by temperature, surface type, and ultraviolet radiation. This information will be useful for evaluating environmental influences on the efficacy of herbicide applications and on the fate of the herbicide. Triclopyr is used in right-of-way, forest, and range vegetation management programs (Gratkowski et al., 1978; Newton et al., 1987; Reynolds et al., 1983). The environmental fate of triclopyr has been investigated in forest soils (Lee et al., 1986), range sites (Norris et al., 1987), and forest vegetation (Newton et al., 1987). There is, however, little information on the short-term environmental distribution of triclopyr from fresh foliar deposits. Foliar penetration, volatilization, and photolysis are short-term processes that determine the initial distribution of triclopyr in forest environments, the treatment efficacy, and the risks of exposing nontarget organisms.

Triclopyr BEE (λ_{max} = 280 nm) in water has a photolysis half-life of about 26 h when exposed to sunlight, and triclopyr BEE's absorbance spectrum significantly overlaps the solar spectrum (McCall and Gavit, 1986). The hydrolysis of triclopyr ester has half-lives of 84, 8.7, and 0.5 days at pH 5, 7, and 9 (25 °C), respectively (McCall and Gavit, 1986). The photolysis rate constant for the acid is 0.128/h, and the rate for the BEE ester is 0.021/h at 35 °C in water. The acid and ester forms are present in a ratio that changes with the rate of ester hydrolysis, and the acid photolysis rate is greater than that for the ester. Consequently, the apparent rate of photolysis of triclopyr BEE substantially depends on the pH of the solution.

Foliar penetration by herbicides has been studied extensively (Bentson, 1990). A few of the general features of foliar penetration by herbicides germane to this study are the following: (1) Nonpolar forms of herbicide penetrate leaf tissues faster than ionic or polar forms (Chamel, 1986). (2) Foliar penetration is more rapid when oil-based formulations are used than when herbicide deposits are polar (e.g., water) (Baker, 1980). (3) Penetration is enhanced when deposits impact stomata, trichomes, cuticle over veins, or petioles, because either these provide a path of entry not protected by the cuticle or the cuticle is thinner than elsewhere on the leaf. (4) Deciduous broadleaf plants absorb greater quantities of herbicide from foliar deposits than do evergreen broadleaves (Riederer and Schonherr, 1985). For these reasons, foliar penetration studies should use the commonly applied tank mix of the herbicide formulation, and foliage should be similar to that of field-grown plants.

Triclopyr foliar penetration has been studied in greenhouse-grown honey mesquite [*Prosopis juliflora* var. glandulosa (Torr.) Cockerell], where 66% of the ester applied in a noncommercial formulation was absorbed by leaves in 24 h (Bovey et al., 1983). Leaf surface characteristics of the evergreen broadleaf tanoak [*Lithocarpus densiflorus* (Hook. and Arn.) Rehd.] that were found to enhance foliar penetration by triclopyr acid in a noncommercial deposit are trichome basal cells, leaf side (abaxial greater than adaxial), the amount of epicuticular wax, and leaf maturity (foliar penetration is greater in young leaves, which is correlated with some of the other features) (King and Radosevich, 1978).

The specific hypotheses tested in this study were as follows: (1) Foliar penetration is the primary process by which triclopyr BEE dissipates from surface deposits on foliage and is dependent on temperature, light, and surface type. (2) Losses of triclopyr BEE in the dark are small and depend on temperature and surface characteristics. (3) Losses of triclopyr BEE in the light decrease foliar penetration.

EXPERIMENTAL SECTION

The dissipation of triclopyr BEE from surface deposits under various environmental conditions was measured in laboratory and outdoor experiments. The surfaces were glass microscope slides and excised leaves of Pacific madrone and giant chinkapin. Madrone and chinkapin were selected because they are common

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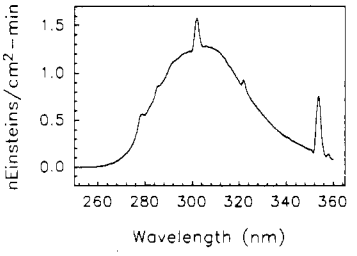

Figure 1. Emission spectrum of Westinghouse FS-40 fluorescent tubes.

targets of triclopyr applications and foliage was available locally and all year. Madrone lack stomata on the upper leaf surface. The upper surfaces of chinkapin leaves have a sparse covering of stellate trichomes and lack stomata. Glass slides were used to measure the dissipation of triclopyr in the absence of foliar penetration.

Laboratory Experiment. Surface deposits of Garlon 4 herbicide on glass slides and leaves were exposed to either light or dark at 10, 25, and 40 °C (a total of six different environmental treatments, each replicated three times) for about 0, 820 (14 h), 1640 (27 h), 2460 (41 h), 3280 (54 h), and 4100 (68 h) min in a controlled-temperature chamber. The study used a four-way factorial split-plot design; the factors were surface type, light condition, temperature, and time. Each replication was run at a separate time. The temperature range was selected to bracket field conditions to which herbicide deposits might be exposed. Each replication had 42 madrone leaves, 42 chinkapin leaves, and 18 glass slides.

Healthy foliage was chosen to exclude surface necroses or insect damage that might increase foliar penetration of triclopyr. Small branches were removed from trees in the field and placed in water until leaves were excised. Surface applications took about 1.5–2 h, and leaves were excised about 2–3 h before being placed in the chamber. Deposits were allowed to dry until they were no longer mobile on the surfaces, which was generally within 1 h after application, and the leaves were placed in the chamber at the same time.

The treatment solution was prepared with 0.165 g of Garlon 4 herbicide [Dow Chemical Inc., Lot MM85022121 (density 1.081 g/mL) containing 44.3% triclopyr ae as the BEE ester] and 13.524 g of water to yield a solution with a triclopyr ae concentration of 5.40 mg/mL. The resultant emulsion is typical of triclopyr tank mixes used in aerial applications in forestry. A new treatment solution was prepared immediately before surface application for each replication. Treatment solutions were continuously stirred during applications. Each surface received a 5-μL drop of the treatment solution. Droplets were placed on the distal half of leaves, between leaf margins and midveins on upper surfaces.

Light was provided by two Westinghouse FS-40 artificial sunlight fluorescent tubes mounted in a standard fluorescent lamp fixture. Output of these in the ultraviolet is like that of solar radiation reaching the Earth's surface at sea level below 45° latitude. Triclopyr BEE absorbance has been shown to overlap significantly with the solar spectrum (McCall and Gavit, 1986). The output of the lamps was measured with an Optronics Laboratories Model 742 discrete band spectroradiometer (Figure 1). Two cyclopentanone actinometers were placed in the chamber to measure UV radiation over each time interval (Mill and Mabey, 1985). Bottoms of the fluorescent tubes were 30 cm from the surfaces. The chamber was a Shearer dual jet controlled-temperature cabinet (Model RT46B-SE).

Leaves (seven of each species) and glass slides (three) were selected at random for removal at each sampling time and immediately rinsed (see Analytical Methods). More leaves than slides were used, because lower and more variable recoveries of triclopyr were expected from leaf surfaces.

Outdoor Experiment. The laboratory data were validated with three outdoor exposures in which triclopyr herbicide deposits were exposed to late-summer ambient light and temperatures for 4160 min, the same time span as in the laboratory experiment. Each outdoor exposure had the same number of leaves and glass slides and sampling times as the laboratory experiment.

The outdoor experiment was conducted in Corvallis, OR (latitude 44° 34′ N, longitude 123° 16′ W, altitude 83 m above sea level). Exposures began on August 4, August 24, and September 21, 1987. Cyclopentanone actinometers were used as in the laboratory experiment to monitor ultraviolet radiation.

Surface Temperature Measurement. In both laboratory and outdoor experiments, surface and air temperatures were recorded. Thermilinear thermoistor composites (Type 44018 Omega Engineering, Inc.) were attached with heat sink grease to three untreated leaves each of madrone and chinkapin and two glass slides. Two thermistors were used to measure air temperature. Each independent set of thermistors was placed in a parallel circuit, thereby giving the mean surface or air temperature. The parallel thermistor circuit was connected to a linear thermistor network circuit (Type 44201, Omega Engineering). Excitation of the thermistors and data collection were by an ICS Micropac 140 data logger.

Surface Deposit Areas. Estimates of the surface area that a deposit covered were made by applying 5-μL drops of the herbicide treatment solution to 100 each of glass slides and madrone and chinkapin leaves. Immediately after the deposits had dried, the visible perimeter of the deposit was traced on sheets of clear acetate. The area within the perimeter was darkened, and the deposit areas were subsequently measured with a leaf area planimeter (Licor Inc.).

Foliar Surface Weights. Leaf weights were believed to change substantially at 25 and 40 °C, because of water loss from excised leaves. To determine whether change in hydration of foliage was correlated with foliar penetration of triclopyr, pretreatment and posttreatment weights were measured. After the herbicide deposit had dried (about 1 h after application), each leaf was weighed to 0.01 g before placement in the chamber. Leaves removed at each sampling time were reweighed before the acetone rinse.

Analytical Methods. *Residues in Surface Deposits.* Each surface was rinsed immediately after removal from treatment conditions with 15 mL of acetone. All rinse acetone of a surface type from a sample time in a replication was pooled in a 150-mL beaker, resulting in 105 mL of acetone rinse for a leaf sample and 45 mL for a slide sample. Acetone was evaporated to about 20 mL and transferred to a 100-mL centrifuge tube. Transfer was completed with two 10-mL acetone rinses of a beaker. Acetone was evaporated just to dryness in the centrifuge tube, and 50 mL of 0.1 N NaOH was added. The centrifuge tube was capped and allowed to stand for 2 days at room temperature to hydrolyze the ester. Just before extraction, 2.5 mL of 6 N H_2SO_4 and 23 g of NaCl were added to the aqueous solution. A rinse sample was extracted three times by shaking the solution for 35 min with 50-mL aliquots of diethyl ether. The organic phase was transferred with a 25-mL pipet to a beaker. The ether extract was evaporated to about 10 mL and transferred to a 45-mL vial. Transfer was completed with three additional 10-mL ether rinses of the beaker. Cleanup and quantification followed the procedure described below for leaf samples.

Residues in Leaf Tissues. The analytical methodology was adapted from Dow Chemical Method ACR 78.11 (Glas, 1978) to improve recoveries with madrone and chinkapin foliage.

One-centimeter strips of the sample leaves were homogenized with 120 mL of 0.1 N NaOH in a Sorvall blender and transferred with a 30-mL rinse of 0.1 N NaOH to a 250-mL centrifuge tube. The centrifuge tube was capped and allowed to stand for 2 days at room temperature to hydrolyze the ester. The centrifuge tube was placed into a boiling water bath for 1 h to further digest leaf tissues, followed by capping and shaking for 30 min. Leaf homogenate was acidified with 2.75 mL of 6 N H_2SO_4 to protonate triclopyr acid residues and cooled, and 30 mL of ether was added to the tube, which was capped and shaken for 10 min. The tube was centrifuged for 8 min at 2000 rpm to break emulsions and separate the phases. The organic phase was transferred to a 50-mL beaker. Extraction was repeated twice, and extracts were combined. The extract was evaporated to 10 mL and quantitatively transferred to a tared 40-mL screw-cap vial (taking care not to transfer any water). The ether extract was adjusted to 20 g in the vial with ether. Five grams of extract was then removed for further cleanup.

The 5 g of extract was adjusted in a beaker to 25 mL with ether and then added to a column containing 2 g (2-cm column packing length) of Woelm basic alumina (3% w/w deactivated with water, prewetted with 2 mL of ether). This column cleanup separated triclopyr acid residues from tissue digestion products and other sample contaminants in the ether extract. The beaker was rinsed with 10 and 20 mL of ether, and the rinses were added to the column. The column was washed with 20 mL of acetone and the eluate discarded. Triclopyr was eluted with 20 mL of 10% v/v of NH_4OH (29% aqueous) in methanol into a beaker. Several carborundum boiling stones were added, and the eluate was evaporated to near dryness on a steam bath. Residue was transferred to a 12-dram vial with 10 mL of deionized water. Vial contents were acidified with 2.5 mL of 6 N H_2SO_4; 2 mL of saturated $KMnO_4$ was added, and the contents were swirled and allowed to stand for 5 min at room temperature to oxidize water-insoluble sample contaminants. Oxidation of sample contaminants rendered them separable from protonated triclopyr acid residues in subsequent extractions. The oxidation reaction was stopped by addition of 5 N $NaHSO_3$ with swirling until the solution was clear and colorless. Triclopyr was extracted from this solution after 5 g of NaCl and 15 mL of ether were added, followed by 10 min of shaking. The extraction was repeated, and the organic phases were combined and evaporated to about 2 mL on a steam bath. Any water present was absorbed by addition of a trace of Na_2SO_4.

Triclopyr was methylated with about 1–2 mL of a 13.7 mg/mL diazomethane in ether solution (until yellow color persisted) and the beaker covered with a watch glass and allowed to stand for 10 min. The watch glass was removed and diazomethane allowed to evaporate; however, the sample was prevented from going to dryness by further additions of ether. Esterified extract was transferred to a column of 1 g (1-cm packed column length) of Woelm basic alumina (3% w/w water deactivated, prewetted with 2 mL of ether), and the beaker was rinsed with 20 mL of ether, which was also added to the column. Column cleanup at this stage separated methylation reaction products from the triclopyr methyl ester. The eluate was evaporated to 2 mL. Eluate was transferred to a vial with three 2-mL aliquots of ether and a single 4-mL wash of hexane. Volume was adjusted by weight to 20 mL.

Detection. Resolution and detection were performed with a Hewlett-Packard 5880 gas chromatograph with a ^{63}Ni EC detector. A 15-m capillary column (J&W Scientific DB1-15W) was used. The carrier gas was hydrogen at a flow of 1 mL/min. Detector makeup gas was 95:5 argon/methane. Injections were made in the splitless mode with the injection port at 220 °C. The oven temperature program was 80 °C for the first 30 s, ramped to 150 °C at a rate of 25 °C/min. Samples were injected by an autosampler set at 2-μL injection volume. Two injections were made of each sample.

Quality Assurance. Three recovery samples were prepared for each surface type and fortified with the Garlon 4 (triclopyr BEE) treatment solution during each treatment replication. Samples were fortified at levels that covered the range of expected concentrations of authentic experimental samples. Blank samples were also occasionally introduced. The analyst did not know the quantity of triclopyr BEE added to samples.

Recoveries of triclopyr BEE from leaves averaged 84 ± 5% and 85 ± 8% for chinkapin and madrone, respectively. Recoveries from deposits averaged 70 ± 3%. Detected sample quantities were adjusted with the recovery results from each treatment replication.

Cyclopentanone Actinometer. Cyclopentanone undergoes photolysis to 4-pentenal over the UV light band triclopyr absorbs. The actinometer solution contained by mole fraction 0.001 cyclopentanone, 6×10^{-4} dodecane, and the remainder cyclohexane. Cyclopentanone actinometer preparation and analysis followed the method of Freeman and Srinivasa (1983).

Statistical Analyses and Modeling. The data from the laboratory study were analyzed as a factorial experiment by using analysis of variance.

Mass balance coefficients (MBCs) were dependent variables in linear regressions of the laboratory data. Other common data transformations were insufficient to linearize the data. We defined the MBCs as

$$K_{Lt} = n_{Lt}/(n_{Dt} + n_{Ft}) \quad (1)$$

$$K_{Ft} = n_{Ft}/(n_{Dt} + n_{Lt}) \quad (2)$$

$$K_{SLt} = n_{Lt}/n_{Dt} \quad (3)$$

Variables for a given time t are defined as n_{Lt} is the amount of triclopyr BEE lost, n_{Dt} is the amount of triclopyr BEE remaining in deposit, and n_{Ft} is the amount of triclopyr BEE in foliar tissues.

The MBCs for leaf surfaces can be solved for the quantity in each compartment by using

$$n_{Lt} = K_{Lt}n_T/(1 + K_{Lt}) \quad (4)$$

$$n_{Ft} = K_{Ft}n_T/(1 + K_{Ft}) \quad (5)$$

where n_T represents the total quantity (moles) of triclopyr BEE in deposits on a specific surface. Equations 4 and 5 were derived by using the equalities

$$(n_{Dt} + n_{Ft}) = (n_T - n_{Lt}) \quad (6)$$

$$(n_{Dt} + n_{Lt}) = (n_T - n_{Ft}) \quad (7)$$

For slides, K_{SLt} is substituted for K_{Lt} in eq 4. The amount of triclopyr left in deposits on glass slides at t can be found with

$$n_{Dt} = n_T/(1 + K_{SLt}) \quad (8)$$

Computer programs were written in BASIC language to model changes in MBCs over time, under varying conditions of temperature and insolation, for each type of surface. The change in the MBCs over a 10-min isothermal time interval were modeled with

$$dK = ((\partial K/\partial t)_T\, dt + (\partial K/\partial I)_T\, dI) \quad (9)$$

where K is an MBC, $(\partial K/\partial t)_T$ is the partial derivative of an MBC with respect to time at constant temperature, and $(\partial K/\partial I)_T$ is the partial derivative of K with respect to incoming radiation, which was solely a function of time in the laboratory experiment. The partial derivatives were taken as derivatives of the appropriate linear regressions. Partial derivatives at temperatures between experimental temperature levels were determined with linear interpolation. It was assumed that changes in the MBCs over time are monotonically nondecreasing functions, because the process is irreversible. Integration of eq 9 for diurnally changing regimes of temperature and light was approximated by summing changes in the MBCs over time. The outdoor exposures were used to determine integration constants and confidence intervals about the model predictions (Reynolds, 1984).

Models were written so that simple field measures could be used as inputs. A minimum–maximum thermometer and some estimate of UV insolation, either from data tables or from direct measurement, are required. The times of minimum and maximum temperatures and times of any isothermal intervals are estimated from knowledge of a site and local weather patterns.

RESULTS

Laboratory Experiment. Excised leaves were observed to dry at a rate that depended on the chamber's temperature. Proportional changes in leaf weight (change in weight/initial weight) were found to contribute to the dissipation of triclopyr BEE from leaf surfaces in linear regressions (Figure 2).

The quantities of triclopyr BEE in deposits decreased as triclopyr BEE penetrated into leaves and was lost from surfaces (Figures 3–5). Losses of triclopyr BEE increased with temperature and with the addition of light regardless of the type of surface. The greatest losses of triclopyr BEE were from glass slides (Figure 3). Foliar penetration of triclopyr BEE increased with a rise in temperature but was more extensive into chinkapin than madrone (Figures 4 and 5). Leaf surfaces contributed greater variability to

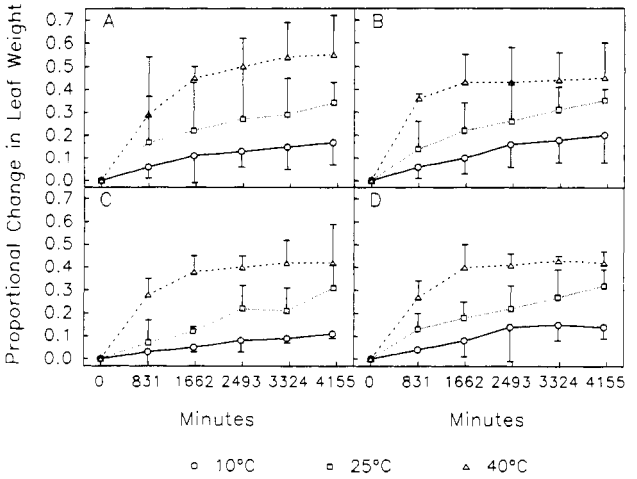

Figure 2. Mean proportional leaf weight change at different treatment temperatures: (A) madrone, dark; (B) madrone, light; (C) chinkapin, dark; (D) chinkapin, light. Vertical bars are half of the 95% confidence intervals.

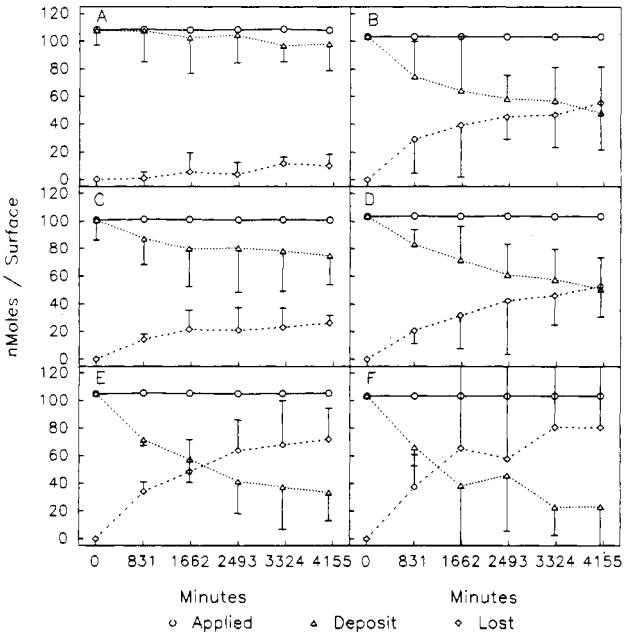

Figure 3. Applied quantities, deposit recoveries, and amounts lost of triclopyr on glass microscope slides. Treatments: (A) 10 °C, dark; (B) 10 °C, light; (C) 25 °C, dark; (D) 25 °C, light; (E) 40 °C, dark; (F) 40 °C, light. Vertical bars are half of the 95% confidence intervals.

measurements than did slide surfaces, as indicated by the 95% confidence intervals (Figures 3–5).

The aqueous Garlon 4 treatment solution was observed to spread to various extents on the different surfaces. The areas that a 5-μL droplet of the treatment solution spread on glass slides and on madrone and chinkapin leaf surfaces were 0.56, 0.10, and 0.30 cm^2, respectively. These deposit areas were used to adjust the photon flux densities intercepted by deposits on the various surfaces.

Factorial Analysis of Variance Results. Analysis of variance results for triclopyr BEE quantities remaining in deposits show two significant ($p \leq 0.001$) three-way interactions: surface by temperature by light, and temperature by time by light (Tables I and II). With significant interactions, main effects are meaningless in analyses of variance.

The surface that a triclopyr BEE deposit was on influenced the subsequent dissipation of the herbicide. Triclopyr BEE quantities in deposits on surfaces signif-

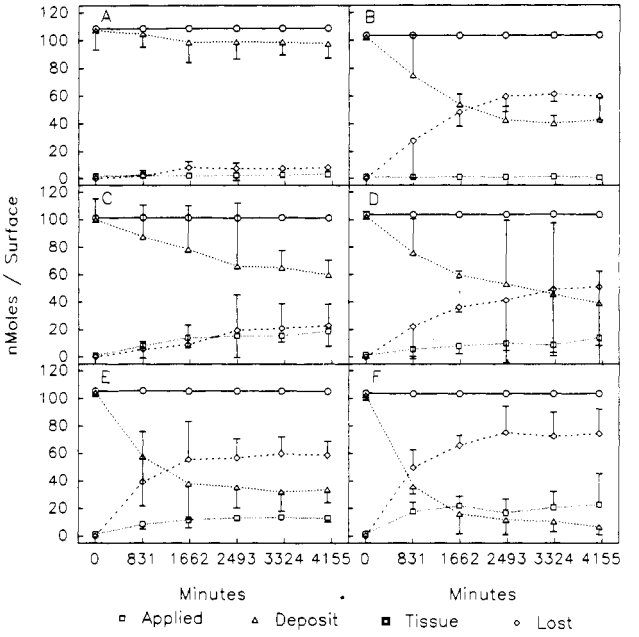

Figure 4. Applied quantities, deposit and tissue recoveries, and amounts lost of triclopyr on Pacific madrone leaves. Treatments: (A) 10 °C, dark; (B) 10 °C, light; (C) 25 °C, dark; (D) 25 °C, light; (E) 40 °C, dark; (F) 40 °C, light. Vertical bars are half of the 95% confidence intervals.

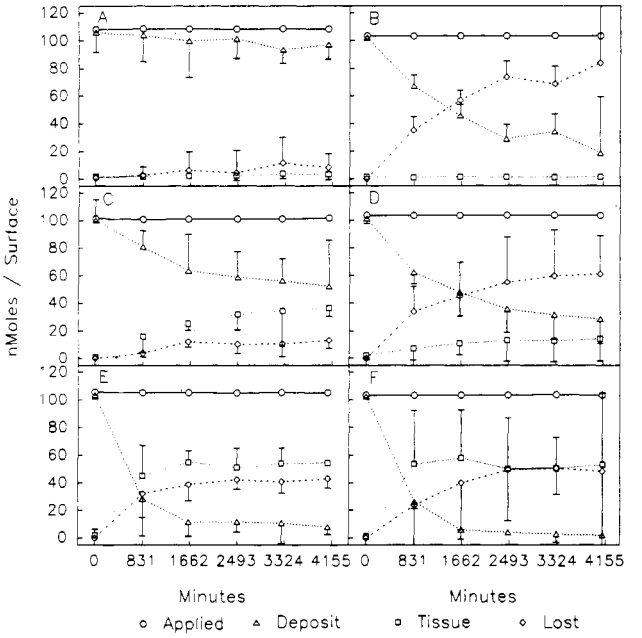

Figure 5. Applied quantities, deposit and tissue recoveries, and amounts lost of triclopyr on giant chinkapin leaves. Treatments: (A) 10 °C, dark; (B) 10 °C, light; (C) 25 °C, dark; (D) 25 °C, light; (E) 40 °C, dark; (F) 40 °C, light. Vertical bars are half of the 95% confidence intervals.

icantly decreased ($p \leq 0.05$) as temperature rose in both the dark and light treatments (Table I). On madrone foliage in the dark, the significant decrease ($p \leq 0.05$) of triclopyr BEE in deposits with rising temperature occurred between 10 and 40 °C, but not between 25 and 40 °C. Comparisons of triclopyr BEE amounts in deposits showed a significant decrease from exposure to light only at 10 °C in each type of surface (Table I). The lack of significant differences between quantities of triclopyr BEE in deposits in the light and dark treatments at 25 and 40 °C is a consequence of greater variability from pooling data of different times. Triclopyr BEE quantities in deposits on chinkapin leaves are significantly less ($p \leq 0.05$) than

Table I. Means for the Interaction of Surface by Temperature and by Light for the Amount of Triclopyr in Surface Deposits for both the Dark and Light Treatments[a]

	surface					
	glass slides		madrone		chinkapin	
T, °C	dark	light	dark	light	dark	light
10	102.65	67.55	100.91	59.54	100.32	52.21
25	83.58	71.27	76.05	62.41	68.57	51.02
40	56.59	50.13	50.12	30.50	28.89	23.77

[a] Units are nanomoles per surface. The means represent values for a 35-h exposure (average over time). The mean square error (MSE) for this analysis of variance is 5.4×10^{-17}.

Table II. Means for the Temperature by Time by Light Interaction for the Amount of Triclopyr in Deposits for the Dark and Light Replications[a]

	dark			light		
h	10 °C	25 °C	40 °C	10 °C	25 °C	40 °C
0	106.97	100.28	104.19	102.54	102.24	102.51
14	105.13	85.19	52.47	72.10	73.66	42.03
27	100.38	73.91	35.53	54.57	59.59	19.43
41	101.65	68.32	29.55	43.26	49.85	19.81
54	96.35	66.51	25.47	43.80	44.86	13.21
68	97.57	62.18	23.98	41.09	39.28	11.82

[a] Units are nanomolar per surface. The means are for an average surface. The mean square error (MSE) for this analysis of variance is 5.4×10^{-17}.

Table III. Means for the Temperature by Time by Surface Interaction for the Amount of Triclopyr Recovered from Leaf Tissues for the Combined Dark and Light Treatments[a]

	surface					
	madrone			chinkapin		
h	10 °C	25 °C	40 °C	10 °C	25 °C	40 °C
0	1.32	1.31	1.42	1.48	1.74	1.59
14	1.60	6.86	13.17	1.52	11.69	49.32
27	1.58	10.99	16.83	1.88	18.11	56.29
41	1.66	12.55	14.93	1.85	22.50	50.58
54	1.97	12.17	17.08	2.38	23.50	52.16
68	1.92	16.31	17.87	2.23	25.23	53.67

[a] Units are nanomoles per surface. The mean square error (MSE) for this analysis of variance is 4.3×10^{-17}.

quantities in deposits on either glass slides or madrone foliage in all 40 °C treatments. Temperature and surface type interactively influence the loss of triclopyr BEE from deposits.

The loss of triclopyr BEE from deposits was affected by the interaction of temperature by light by time (Table II). The quantities of triclopyr BEE in deposits at 54 and 68 h were significantly ($p \leq 0.05$) less than at 14 h in the 25 and 40 °C treatments. The amount of triclopyr BEE in deposits at 14 h in the 10 °C light treatment was significantly ($p \leq 0.05$) greater than at all later times. Without light, however, quantities of triclopyr BEE in deposits did not differ significantly over time at 10 °C. The quantity of triclopyr BEE in deposits at 14 h in the 25 °C light treatment was significantly ($p \leq 0.05$) greater than deposit recoveries 41 h and later. The 14-h deposit recoveries in the 40 °C light treatment are significantly greater than the 54- and 68-h recoveries. Both greater light and temperature increase the rate of triclopyr BEE loss from surfaces.

Analysis of variance of the triclopyr BEE quantity in leaf tissue (foliar penetration) showed a single significant ($p \leq 0.001$) three-way interaction term: temperature by time by surface (Table III). Ultraviolet light did not affect foliar penetration by triclopyr BEE. Foliar penetration of triclopyr BEE into chinkapin at 40 °C was more than

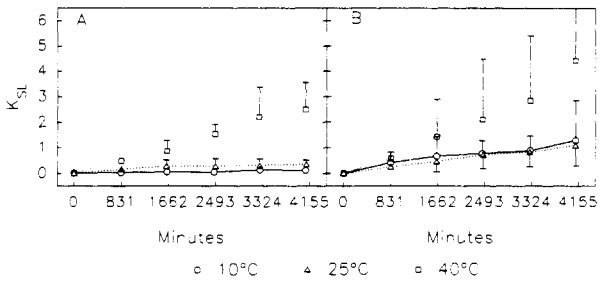

Figure 6. Mean mass balance coefficient (K_{SL}) at different temperatures and times for triclopyr deposits on glass microscope slides. Treatments: (A) dark; (B) light. Vertical bars are half of the 95% confidence intervals.

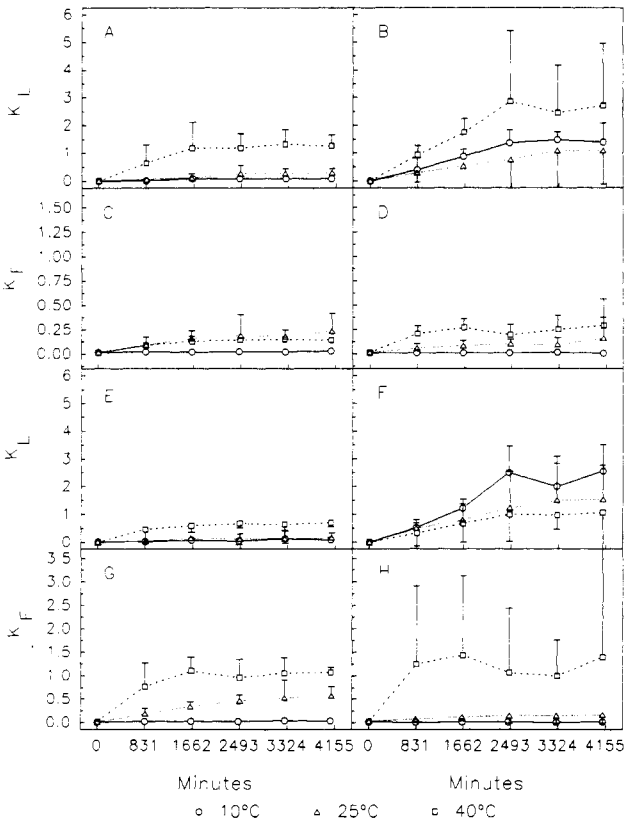

Figure 7. Mean mass balance coefficients, K_L and K_F, at different temperatures and times for triclopyr deposits with Pacific madrone and giant chinkapin leaves. Treatments: (A) K_L madrone, dark; (B) K_L madrone, light; (C) K_F madrone, dark; (D) K_F madrone, light; (E) K_L chinkapin, dark; (F) K_L chinkapin, light; (G) K_F chinkapin, dark; (H) K_F chinkapin, light. Vertical bars are half of the 95% confidence intervals.

2 times greater (significantly different at the $p \leq 0.01$ level) than its penetration into madrone leaves. The quantity of triclopyr BEE in leaf tissues was least at 10 °C. Comparison of triclopyr BEE quantities in madrone and chinkapin tissues at 10 °C showed no significant difference. Foliar penetration of triclopyr BEE was rapid with no significant differences in quantities between 14 h and later sample times.

Mass Balance Coefficients. The MBCs formed nearly straight lines between the beginning of dark treatment exposure and 27 h, except in the case of glass slides at 40 °C (Figures 6 and 7). Significant ($p \leq 0.01$) linear regressions were obtained for all MBC lines to 27 h, except K_L and K_F for chinkapin leaves at 10 °C, which are constant after 14 h. The variables that explained the most variation in the MBCs were (1) elapsed time, (2) the naperian log of elapsed time, and (3) the proportional change in leaf weight. Mean values were used to approximate MBCs

Table IV. Environmental Conditions of the Outdoor Exposures

exposure date and minutes	T_{max}, °C	T_{min}, °C	cum light[a]
Aug 4, 1987			
0	35	11	0.0
831	32	11	6.2
1662	32	11	17.4
2493	27	9	18.9
3324	27	9	30.9
4155	27	12	32.7
Aug 24, 1987			
0	32	8	0.0
831	31	8	4.9
1662	31	8	14.8
2493	32	12	15.3
3324	32	12	24.8
4155	33	10	27.0
Sept 21, 1987			
0	29	7	0.0
831	30	7	0.6
1662	30	7	9.2
2493	33	9	9.6
3324	33	9	14.7
4155	24	8	15.4

[a] Cumulative μEinsteins/cm² as detected by cyclopentanone actinometers.

after 27 h, since there were no significant linear relations after that time. Regressions were performed on the proportional change in leaf weight, so that this variable could be included in models.

The difference between a MBC in light treatments from the MBC in the dark treatments at the same time and temperature was used to determine the influence of UV light on the MBCs. The differences were all significant [$p \leq 0.05$ (most show a $p \leq 0.01$)] by linear regression analysis, except for the differences in triclopyr BEE distribution associated with K_L of chinkapin at 40 °C and K_F of chinkapin at 10 and 40 °C.

The MBC adjustment equations for light treatment are

$$K_{SL}(\text{light}) = K_{SL}(\text{dark}) + e^{cI} \quad (10)$$

$$K_L(\text{light}) = K_L(\text{dark}) + dI + f(P) + g(\log E) \quad (11)$$

$$K_F(\text{light}) = K_F(\text{dark}) + e^{(hI+i(\log(E))+j(P))} \quad (12)$$

The variables c, d, f, g, h, j, and k are regression parameters for the variables that follow them, I, P, and E, which are cumulative photon density (Einsteins/cm²), proportional leaf weight change, and elapsed treatment time (minutes), respectively.

Outdoor Experiment. The first outdoor exposure began on August 4, 1987, at 13:54 (all times are PDT) in clear weather. The next day was clear with a slight amount of morning dew; however, partly cloudy conditions were present from 15:00 to 17:00, and strong winds occurred from 15:00 until nightfall. August 6 was foggy until 11:00; afternoon winds resumed at 15:00 and lasted until nightfall (Table IV).

The second exposure began on August 24 at 14:12 under clear skies. Light winds blew throughout August 25, and at 16:00 there were haze and high clouds. August 26 was about 40% overcast from high clouds (Table IV).

The third exposure began on September 21 at 16:30 (Figure 9). There were no clouds, but smoke haze was present from forest fires 400 km to the south. The following day also had smoke haze. Morning fog on

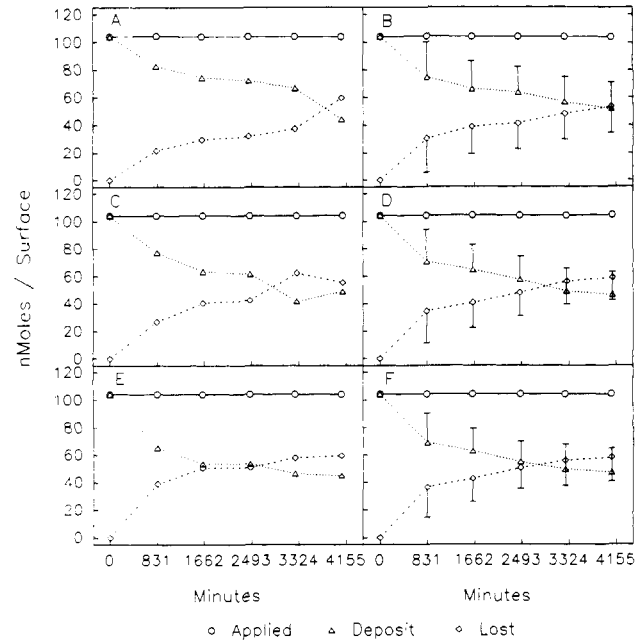

Figure 8. Results and predictions for outdoor-exposed glass microscope slides: (A) actual results Aug 4, 1987; (B) predictions Aug 4, 1987; (C) actual results Aug 24, 1987; (D) predictions Aug 24, 1987; (E) actual results Sept 21, 1987; (F) predictions Sept 21, 1987. Vertical bars are half of the 95% confidence intervals.

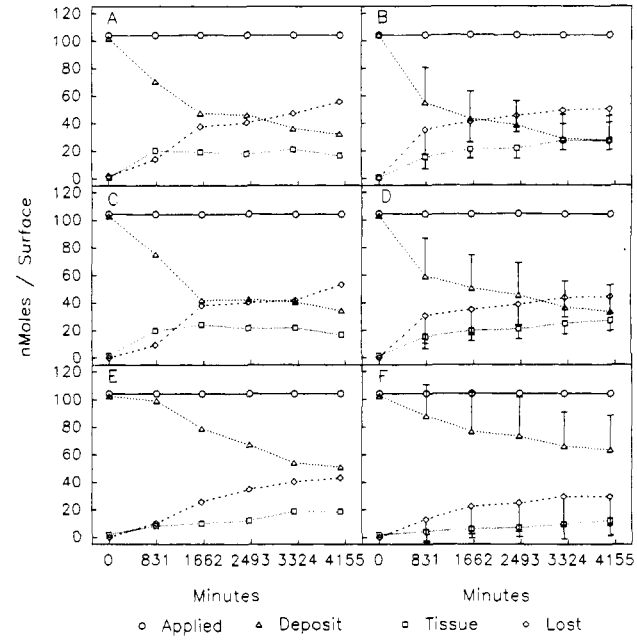

Figure 9. Results and predictions for outdoor-exposed Pacific madrone leaves: (A) actual results Aug 4, 1987; (B) predictions Aug 4, 1987; (C) actual results Aug 24, 1987; (D) predictions Aug 24, 1987; (E) actual results Sept 21, 1987; (F) predictions Sept 21, 1987. Vertical bars are half of the 95% confidence intervals.

September 23 dissipated before sunup, but smoke haze was present. Winds began about 16:00, and dew was on surfaces at 22:00. On September 24 fog lasted until the end of the exposure, and morning dew dissipated by 12:00.

Foliage temperatures averaged about 5 °C greater than the ambient air temperature from insolation during the daytime. Glass microscope slides had maximum temperatures near the ambient maximum air temperature. The observed results and model predictions agree within 95% confidence intervals (Figures 8–10).

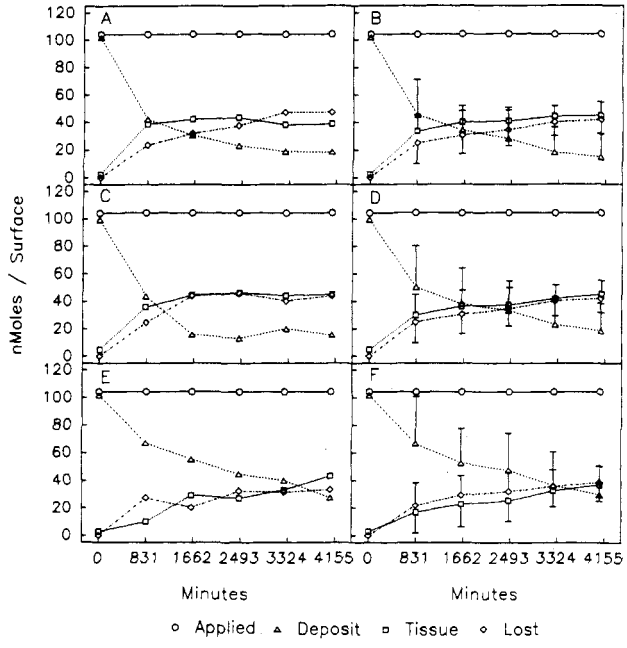

Figure 10. Results and predictions for outdoor-exposed giant chinkapin leaves: (A) actual results Aug 4, 1987; (B) predictions Aug 4, 1987; (C) actual results Aug 24, 1987; (D) predictions Aug 24, 1987; (E) actual results Sept 21, 1987; (F) predictions Sept 21, 1987. Vertical bars are half of the 95% confidence intervals.

DISCUSSION

Laboratory Experiment. *Losses in the Dark.* Short-term triclopyr BEE loss from foliage can be by volatilization, photodegradation (only in light), and metabolism. Although thermal reactions of triclopyr BEE with surface constituents might occur, we do not believe such reactions cause detectable losses given the chemistry of the herbicide.

Surfaces have the ranks according to triclopyr BEE loss in the dark of slides > madrone > chinkapin; however, only chinkapin differs significantly from the other two at 40 °C. The lower loss of triclopyr BEE from chinkapin than from madrone may occur for two reasons: (1) greater foliar penetration by triclopyr BEE into chinkapin than madrone foliage leaves less triclopyr BEE available for loss from deposits on chinkapin or (2) there is greater metabolism of triclopyr BEE in madrone than in chinkapin tissues. Losses from glass slides (impenetrable surface) are greater than from either madrone or chinkapin leaves, presumably because triclopyr BEE remains available for volatilization from deposits.

Losses in the Light. Foliar penetration and loss of triclopyr BEE were least in the 10 °C dark treatment than in any other treatment. Exposure to UV radiation in the 10 °C light treatment caused significantly greater losses of triclopyr BEE from all surfaces than in any other treatment. These results demonstrate the importance of ultraviolet light on the ultimate environmental fate of triclopyr BEE in the absence of other processes (e.g., volatilization, foliar penetration). The effect of UV light is difficult to separate from other processes at temperatures greater than 10 °C, where an unknown quantity of triclopyr BEE was lost from volatilization and metabolism.

No attempt was made to measure products of photodegradation. Photodegradation of triclopyr BEE in sunlight has been demonstrated in aqueous systems (McCall and Gavit, 1986). The quantum yield of triclopyr in the deposit environment relative to actinometer measurements can be estimated with an equation in Mill and Mabey (1985). The deposit volume after evaporation of water was estimated to be 54.5 nL, and the exposed actinometer solution volume was 13.6 mL. These values were used to adjust the results by a factor of 4.0×10^{-6} for the proportionate volumes of deposit versus the actinometer solution. From the data of triclopyr BEE loss from glass microscope slides at 10 °C in the light, the temperature at which there was minimal dissipation of triclopyr in the dark, the quantum yield of triclopyr in the deposit environment was $1.7 \times 10^{-4} \pm 5 \times 10^{-5}$. This is lower than the quantum yield ($8.4 \times 10^{-3} \pm 8 \times 10^{-4}$) found by McCall and Gavit (1986) of triclopyr BEE in water at pH 5, with 0.005 M phosphate buffer at 35 °C. Apparently, the deposit environment decreases the quantum yield of triclopyr BEE photolysis relative to its photolysis quantum yield in water.

Foliar Penetration. Foliar penetration by triclopyr BEE into chinkapin tissues is greater than into madrone foliage (Table III). This may be a consequence of greater deposit spreading on chinkapin leaves than on madrone leaves. Larger deposit areas over leaf surfaces result in a greater tissue volume underlying deposits than with smaller deposit areas. The smaller volume of leaf tissue under small deposit areas would absorb less herbicide than the larger volume of tissues under deposits of more extensive areas and may be the bases for enhanced efficacy with greater spray coverage. The amount of triclopyr BEE penetrating madrone is not significantly different between 25 and 40 °C, but for chinkapin the change in temperature causes nearly a doubling in foliar penetration (Table III). This may be because a smaller deposit area on madrone results in a smaller tissue volume being saturated at 25 °C, and no further triclopyr BEE can enter madrone tissues when the temperature is increased from 25 to 40 °C. Morphological characteristics also play a role, because there is evidence that deposits over veins, basal cells, or trichomes and the thickness of the epicuticular waxes influence the extent of penetration observed on different species (Baker, 1980; King and Radosevich, 1978). Greater deposit spreading on chinkapin surfaces would increase the likelihood of deposits contacting one of these morphological features.

Loss of triclopyr BEE from deposits in the light decreases the amount of triclopyr BEE that was detected in chinkapin foliage at 25 °C (Tables I and III). A decrease in the amount of triclopyr BEE in deposits from photodegradation would lower the concentration gradient between deposits and tissues, thus reducing foliar penetration. Photodegradative losses at 40 °C had no effect on foliar penetration in either madrone or chinkapin. The rate of foliar penetration by triclopyr BEE may be too fast at 40 °C for the concentration gradient between the tissues and the deposit to be impacted greatly by photodegradation.

Proportional Change in Leaf Weight. The proportional change in leaf weight is a significant parameter in the regressions for both madrone and chinkapin MBCs. The reasons that change in proportional leaf weight is significant are (1) a decrease in hydration may open cracks in epicuticular waxes from tissue shrinkage, allowing more triclopyr BEE to enter tissues, and (2) a decrease in hydration would increase the proportion of the organic tissue phase versus the proportion of the hydrated tissue phase, thereby increasing the relative volume that triclopyr BEE could partition into. Whether change in leaf weight is merely a well-correlated artifact of temperature and time or has a real effect on triclopyr BEE dissipation will require further study.

Temperature. The ultimate environmental distribution

of triclopyr BEE is highly influenced by temperature. The amount of triclopyr BEE loss in the dark increases with a rise in temperature. On the other hand, triclopyr BEE loss is greater at lower temperatures in the light but not at higher temperatures, as discussed above. Temperature also significantly affects foliar penetration, particularly in chinkapin foliage.

Outdoor Experiment. The laboratory experiment treatments were conducted at constant temperatures and UV light intensity, while the outdoor experiment temperatures and light regimes varied diurnally. Consequently, triclopyr BEE on slides in the outdoor experiments was lost more rapidly during the warm daytime than at night when temperatures were cooler and UV insolation was absent (Figure 8). Initial losses from glass slides were rapid; however, in the second daylight segment of the exposure, losses were much slower. A slower rate of triclopyr BEE loss from slides in the second daytime period may be the result of (1) the remaining triclopyr BEE being shielded from UV insolation by triclopyr and formulation degradation products near the deposit's surface, (2) the chemical potential of triclopyr BEE in the deposit being nearly equal to that of triclopyr BEE in the atmosphere (Bentson, 1990), (3) loss of formulation components reducing the diffusion of triclopyr BEE from the deposit to the atmosphere, and (4) crystallization of triclopyr BEE in the deposit.

The foliar penetration of triclopyr BEE was rapid in the outdoor exposures. Foliar penetration of triclopyr BEE into chinkapin and madrone leaves occurred almost completely within the first 14 h of exposure (Figures 9 and 10). Results from the outdoor exposures are very similar to those observed in the laboratory experiment. Results from the outdoor exposures indicate that under field conditions the temperature regime in the first 14 h after application determines the extent of foliar penetration and the ultimate internal dose that some forest weeds receive.

Models. The results of model predictions for the three outdoor exposures on the different surface are shown in Figures 8–10. The vertical 95% confidence interval bars were derived by using the technique of Reynolds (1984). The confidence intervals decreased with time, which indicates that there is less variability in predictions as the disposition of triclopyr BEE proceeds. This appears to be an artifact of the confidence interval estimation method since this trend is not apparent in the laboratory data. Results from the outdoor exposures fell within the 95% confidence intervals of the predictions.

The models, however, tend to underpredict loss of triclopyr BEE from deposits, particularly when dew formed on surfaces. Dew was observed on surfaces during several days of the September 21 exposure. Dew has been noted to increase the losses of DDT and toxaphene from deposits (Willis et al., 1980). Humidity may also influence the disposition of triclopyr BEE from leaves and glass slides. This factor was not included in the study but should be considered for inclusion in similar studies in the future.

CONCLUSION

This study demonstrates the importance of temperature in the environmental disposition of triclopyr BEE from deposits. A rise in temperature caused an exponential increase in triclopyr BEE loss and an increase in foliar penetration, depending on species. Triclopyr penetrates the foliage of some plant species more readily than others, as shown by the results for chinkapin and madrone. This may be the basis for some selectivity of the herbicide in evergreen broadleaf species; however, the concentration at sites of action in tissues and metabolic degradation are probably more important in selectivity. Penetration is greatly enhanced by temperatures above 25 °C for some species. On surfaces where foliar penetration is low or nonexistent, triclopyr loss is greater than on surfaces where more penetration occurs.

Foliar penetration may deviate from these results if a different spray mix is used. For instance, it is a common practice in Oregon to prepare a spray mix of 60% diesel oil, 38% water, and 2% Garlon 4 (by volume). This mixture may enhance foliar penetration by disrupting epicuticular waxes, or it may decrease penetration if the partitioning between the deposit and leaves is made less favorable by greater quantities of organic materials in the deposit.

The first hypothesis, that foliar penetration is the primary process by which triclopyr diffuses from foliar deposits, was true for chinkapin at 25 and 40 °C on the basis of the dark treatment results. With madrone leaves, the amount of triclopyr lost from the deposit was greater than the amount that penetrated the leaves; hypothesis 1 therefore was not true for madrone foliage. Losses of triclopyr BEE from madrone leaves in the dark were similar to losses from glass slides, because most of the triclopyr remained in surface deposits on both surfaces.

The second hypothesis, that triclopyr BEE disappearance from deposits on foliage was secondary to foliar penetration, held for chinkapin foliage but not madrone leaves. This demonstrates that with greater foliar penetration triclopyr loss is reduced. Exposure of triclopyr BEE in herbicide deposits to UV light significantly reduces the quantity of triclopyr in surface deposits versus the dark. This suggested that in situ photodegradation may be a significant path of loss for triclopyr on foliar and impenetrable surfaces when other processes are not in operation (e.g., wash-off, metabolism, volatilization).

The protocol of this study provided data that would otherwise be difficult to obtain for forest vegetation. When facilities are not available, vegetation has different foliar properties when young, vegetation is of large stature and difficult to grow, or outdoor-grown foliage differs from greenhouse-grown foliage, then the protocol used herein can yield results that are otherwise unattainable. The use of authentic formulations and surfaces as occur in the field provides data that are useful in models. Although the experimental protocol used here will not supplant field studies, results from these types of studies can enhance the interpretation of patterns of foliar residue dissipation seen in the field.

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Supplementary Material Available: Tables of the regression coefficients, regression statistics, and variable units for regressions of the mass balance coefficients; the inputs for model simulations of the outdoor exposures of times, temperatures, and UV radiation input; and the differences between model predictions and observed outdoor exposure results for each surface (12 pages). Ordering information is given on any current masthead page.

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