Deposition and Dissipation of Three Herbicides in Foliage, Litter, and Soil of Brushfields of Southwest Oregon

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The herbicides 2,4-D ((2,4-dichlorophenoxy)acetic acid), triclopyr ([(3,5,6-trichloro-2-pyridinyl)-oxy]acetic acid), and picloram (4-amino-3,5,6-trichloro-2-pyridinecarboxylic acid) were applied by helicopter to test grids in mountainous southwestern Oregon brushfields on shallow, rocky, clay loam soils. Herbicide concentrations were observed in crown twigs and foliage, browse twigs and foliage, litter, and soil. Initial deposits in the target area ranged from 61 to 115% (average 82%) of the nominal dosage, with coefficients of variation of 29–104%. Initial concentrations in crown foliage were 44 mg/kg for each kilogram per hectare applied; deposits on browse foliage and litter were 38% and 74%, respectively, of crown concentrations. Early after application, decreases were more rapid for salt formulations than for esters. After 79 days, decrease of all herbicides was slight in foliage, but continued in soil. Picloram disappeared most rapidly and was least mobile, followed by triclopyr and 2,4-D. Triclopyr and 2,4-D remained nearly constant in foliage through winter. Disappearance was rapid in litter.

The success of aerial herbicide application in agriculture and forestry has led to its widespread adoption for weed control (Walstad and Kuch, 1987). But such application blankets a target area. Knowledge of where a herbicide lands and in what amounts, and of the persistence and mobility of residues and their potential to harm nontarget species, is central to their evaluation. "Hot spots" and "skips" are of interest for evaluating both hazard and control of target species. A herbicide deposit may persist indefinitely, for some reason inaccessible to microbial breakdown; be broken down by microorganisms that use it as an energy source; move off target through evaporation, surface flow, or leaching; be consumed by herbivores and redistributed in waste products (although little in carrion); or be destroyed abiotically by solar radiation or chemical hydrolysis. This paper reports research on the deposition patterns, persistence, and mobility of three herbicides in a forest ecosystem and assesses the potential for risk.

Newton et al. (1984) reported that a glyphosate release over a tall hardwood forest in Oregon deposited approximately 100 mg/kg in deciduous foliage for each kilogram per hectare released. They devised a model describing deposits in the lower crown and at ground level in terms of interception by foliage above. At the point of interest, interception above is

$$I = 100(1 - {}^{1}/_{2}{}^{L}) \quad (1)$$

where I = percentage of spray intercepted and L = leaf area index (m^2 of leaf area (one surface)/m^2 ground area).

The model predicts that each square meter of foliage per square meter of ground area intercepts about half of the spray penetrating the foliage above. With 3 m^2/m^2 leaf area, one-eighth of the nominal amount would be deposited, and a 5 m^2/m^2 leaf area would intercept about 97%.

Much research has been done on degradation of phenoxy herbicides and picloram (4-amino-3,5,6-trichloro-2-pyridinecarboxylic acid), particularly in soil. Reviews by Altom and Stritzke (1973), Merkle et al. (1973), and Norris (1981) indicate that phenoxy herbicides and picloram are decomposed by microbial activity and that 2,4-D ((2,4-dichlorophenoxy)acetic acid) decomposes much more rapidly than picloram. Triclopyr ([(3,5,6-trichloro-2-pyridinyl)oxy]acetic acid) has been less studied, but its structural resemblance to 2,4,5-T ((2,4,5-trichlorophenoxy)acetic acid) suggests that its behavior should be similar. Conditions favoring microbial activity appear to increase herbicide degradation. Under uniform conditions (particularly in the laboratory), rates of breakdown approach first-order kinetics, but in the field, trace residues tend to persist longer than true first-order kinetics would predict. Rates of loss are generally independent of soil type or reaction if organic matter is sufficient to develop adequate populations of microorganisms and if temperatures and moisture levels are suitable for metabolism.

Conditions analogous to the laboratory studies in which these generalizations have been developed do not exist in the field. Extreme variability is the rule. The environmental extremes of the Siskiyou Mountains of Oregon and northern California, the area of this study, are notable even among forest and mountain sites. The habitats occupied by sclerophyll vegetation are too dry in summer and too cold in winter for substantial contributions to microbial degradation. Rainfall is heavy in winter. Solar radiation is intense in summer, a condition producing maximum solar decomposition but low microflora activity. Such conditions suggest that we should determine degradation empirically, rather than by a kinetic model. We can postulate mechanisms of breakdown, but the mechanisms will be of little value for prediction without detailed microenvironmental data. Rather, many observations over a range of representative environments may give useful estimates of the ranges of persistence and locations of residues.

Interpretation of herbicide persistence as a potential hazard requires knowledge of its availability over time. As concentrations decrease in various parts of the ecosystem (or transfer to other parts), a time × concentration integration will provide a measure of exposure to herbivores and soil inhabitants. Little will be inferred here about higher trophic levels because the herbicides under study are retained in animal tissue, including that of human beings, only briefly (Hay et al., 1974; Hay, 1978; Newton and Dost, 1984). In this paper we report the

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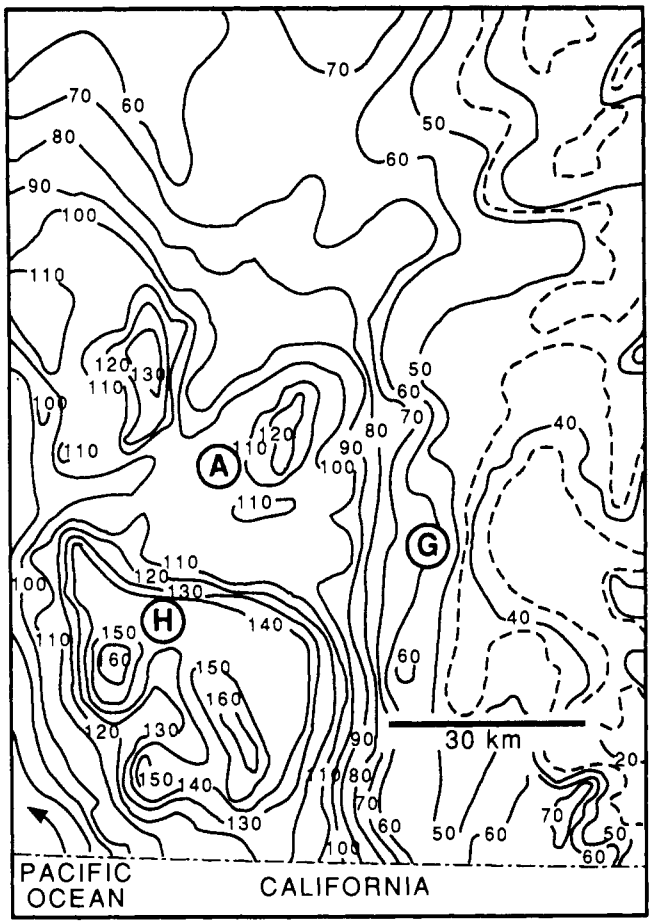

Figure 1. Site locations (A, Agness; G, Galice; H, Hunter Creek) and average annual precipitation (inches per year) in the vicinity of the study area (Froehlich et al., 1982).

arrival and disappearance of residues above and below ground and evaluate the potential impact on nontarget portions of the ecosystem.

MATERIALS AND METHODS

Sites. The three sites (replications) in the Siskiyou Mountains of Oregon were occupied by 5- to 8-year-old vegetation representative of competing vegetation developing after clearcutting and replanting in the region. The sites (Figure 1) were as follows.

Galice. Section 30; T.36 S., R.7 W. W.M.; 720-m elevation, 1200 mm of precipitation. Soils: residual gravelly clay loams derived from mixtures of metasedimentary and serpentine rocks, 45–75 cm deep. Slopes 20–80%.

Agness. Parts of sections 11, 12, and 22; T.35 S., R.11 W. W.M.; 900-m elevation, 2300 mm of precipitation. Soils: residual clay loams derived from metasedimentary rocks, 45–75 cm deep. Slopes 25–45%.

Hunter Creek. Parts of sections 17, 18, and 19; T.37 S., R.12 W. W.M.; 1050-m elevation, 3500 mm of precipitation. Soils: residual clay loams derived from mixtures of metasedimentary rocks, 40–90 cm deep. Slopes 15–80%.

Precipitation varies markedly among the sites in amount, but not in seasonal distribution. Johnsgard (1963) and Froehlich et al. (1982) note that 87% of the precipitation occurs from October through April and that summer months are low in cloud cover and relative humidity and high in solar radiation. From nearby stations (U.S. Weather Bureau, 1980–81), we developed estimates of precipitation for the Agness (Gold Beach) and Galice (Cave Junction) sites during the 11 months after treatment with herbicides (Figure 2).

Galice (a "dry" site) receives 87% of its moisture as rain between mid-October and mid-April. Agness (an intermediate site) receives rainfall in the same distribution (Johnsgard, 1963; Froelich et al., 1982), but the total more nearly represents the

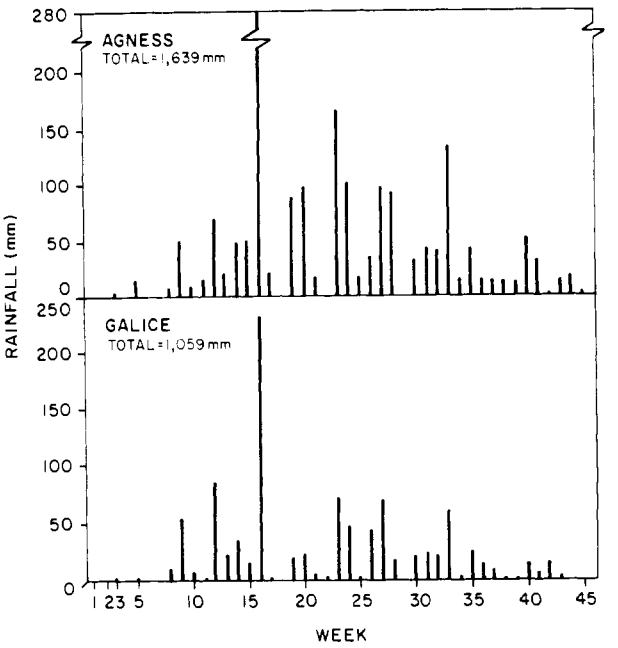

Figure 2. Weekly rainfall at weather stations near Agness and Galice during the 11 months after Aug 13 aerial applications of herbicides (U.S. Weather Bureau, 1980, 1981).

average of the western Siskiyous and California coast range. Hunter Creek (a "wet" site) has similar distribution, a major portion occurring from December to February as snow. The site did not have a nearby weather station, so we estimated total rainfall from an isohyetal map (Figure 1) and assumed that rainfall distribution was similar to that of the nearest recording station.

Vegetation on the three sites was similar, dominated by sprouts of tanoak (*Lithocarpus densiflorus*) 2–3 m tall. The sites had been occupied from 5 to 8 years previously by large, mature Douglas-fir (*Pseudotsuga menziesii*) with a tanoak understory. Mixed with the tanoak were hairy manzanita (*Arctostaphyllos columbiana*), Pacific madrone (*Arbutus menziesii*), varnishleaf caenothus (*Ceanothus velutinus* var. *laevigatus*), ocean spray (*Holodiscus discolor*), and numerous seral herbs and minor shrub species. Canopy density was about 60%, including crowns of planted Douglas-fir.

Treatments. Treatments represented those that foresters might select for weeding conifer plantations or for preparing sites for planting:

chemical	kg/ha
2,4-D, propylene glycol butyl ether esters	3.3
2,4-D, propylene glycol butyl ether esters with picloram as the potassium salt	2.2 ± 0.6
triclopyr, triethylamine salt	2.2
triclopyr, triethylamine salt	4.4
triclopyr, butoxyethyl ester	1.65
triclopyr, butoxyethyl ester	3.3

All herbicides were applied in late summer, August 13 and 14. All were applied by helicopter in water (a total of 120 L/ha spray mixture) through RD-7-46 nozzles that delivered a median drop size (volume weighted) of about 780 μm (Yates et al., 1984). Treatments were applied to 100 × 200 m plots in six adjacent swaths as nearly as possible along the contour of the mountainous terrain. Each treatment was applied to one plot in each of the three sites in a randomized complete-block experiment. The experimental unit was the whole-plot mean for foliage, litter, and soil residues but was the individual subsampling point observation for deposition.

Sampling Procedures. From measurements of initial residues, which give a reasonable approximation of the amount of herbicide entering the target area and of vertical distribution in the canopy, litter, and soil, we estimated flow-through and dissipation in place.

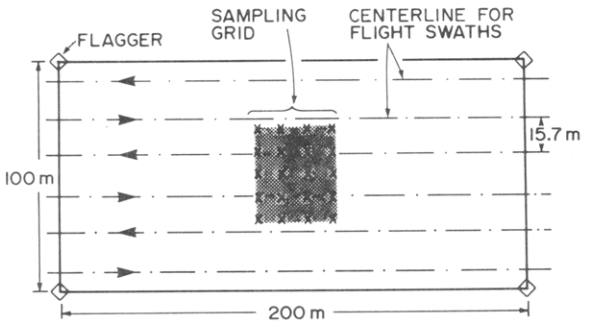

Figure 3. Plot layout showing 20-point sampling grid (shaded) and helicopter flight swaths (direction of flight indicated by arrows on swath centerlines).

Before treatment, tanoak sprout clumps 2–3.5 m tall were located in a rectangular sampling grid in each plot, for 20 observations per treatment on each site (total 480 points). The sample bushes were spaced 10 m apart in a pattern of 4 × 5 sampling points (30 × 40 m) (Figure 3). Sampling was restricted to tanoak bushes because they provided the most consistent medium for composite collections of plant material. They represented both a major portion of the plant cover and a widespread weed problem.

Two branch clusters of sample material in each shrub crown and browse layer (lower crown 30–90 cm above ground) were identified before treatment for later estimates of absolute deposition rate, change of concentration in the foliage with time, and difference in concentration between the upper crown and browse zone. In the middle of each crown branch cluster, a 9-cm metal gill cup with sealable lid was oriented horizontally to catch aerial deposits.

Next to the gill cup, a branch was selected with at least seven current year twigs, each with 7–15 leaves. Each twig was tagged with a future sampling date. This procedure was repeated at the browse line nearly or directly below the crown samples. On each sampling date, a single twig was collected from each layer of each tagged bush. Twigs from each level from each 20-sample plot were coposited and frozen.

Litter (leaves, twigs, and recognizable plant parts deposited within the last several years) was collected from a 0.5 × 0.5 m area beneath each of two randomly selected, tagged bushes and then combined to represent the whole plot and frozen.

Crown samples from pretagged branches and litter samples were collected on the day before treatment, within 1 h after the spray dried on the day of treatment (day 1) and on days 18, 37, 79, 153 and 325 after spraying. Browse layer samples were collected on all but day 18.

Soil samples were collected in each plot from two pits randomly located in parts of the sampling grid not covered by vegetation, in order to minimize interception. Samples were taken at each sampling date from the same general soil column in order to avoid variability attributable to initial differences in deposition and to provide a series following a known starting condition. A straight-shank shovel was used to prepare the pits with a flat side oriented so that rain and mud would not wash down the surface. After 5–10 cm of old surface was removed, equal proportions of soil 5 cm thick were sliced vertically from depths of 0–15, 15–30, and 45–60 cm. On sites with less than 60 cm of soil, we took samples from the bottom 15 cm, which was always between 30 and 60 cm. Only a light shower (<0.25 mm) fell before the first sampling date on day 37, so only the surface 15 cm was sampled then. On days 79, 153, and 325, soils were collected from each pit at each depth. Samples from the two pits per plot were combined in the field and frozen, pending analysis. Rocks were screened out before analysis.

The litter samples were taken beneath tanoak bushes, as the only consistent source of leaf and twig detritus. Soil samples were taken from areas of no cover, as assurance of a maximum deposit from which residue degradation could be followed without secondary input from throughfall. Thus, the soil samples do not reflect conditions beneath the litter samples, but each set reflects maximum levels of contamination.

Analytical Procedures. General methodology for chemical analysis was adapted from Dow Chemical Method ACR 78.11 (Glas, 1978). Gill cups were extracted and analyzed directly, but distinct cleanup procedures were used for analyses of plant material and litter and soil. All were run by gas–liquid chromatography with electron capture detectors. Procedures and recoveries for gill cups, plants, litter, and soil varied as follows.

Gill cups were removed from the freezer and warmed to ambient temperature. Seals were inspected and the outside surfaces sprayed with a 0.1 N solution of sodium hydroxide. The cups were rinsed after a few minutes with cold tap water and dried with a paper towel.

Each gill cup sample was fortified with 5 μL of a spike solution containing 20 mg/L of 2,4,5-T acid (100 pg), the internal standard, added with a 10-μL gas-tight syringe. Backup in the syringe was 2 μL of acetone and 1 μL of air, and the spike column was recorded to the nearest 0.01 μL. After fortification, the insides of each cup were rinsed twice into a glass bottle with 5–8 mL of acetone, which was evaporated just to dryness with high-purity nitrogen. The cups were then rinsed with 100 mL of 0.1 N sodium hydroxide, resealed, and shaken 30 min at 100 cycles/min. The sodium hydroxide was then added to the glass bottles containing the evaporated acetone, and the bottles were capped and stored.

Five grams of the sodium hydroxide–herbicide solution was added to a tared 40-mL vial, with 3.5 g of sodium chloride, 0.5 mL of 6 N sulfuric acid, and 10 mL of 3/7 ether/hexane (v/v). Each vial was capped, shaken for 5 min at 280 cycles/min, and centrifuged for 1–2 min at 2000 rpm to separate the phases. One milliliter of the organic phase was transferred to a 10-mL vial and then methylated with 0.25–0.50 mL of a solution of diazomethane in ether (18 mg/mL). After methylation, 2 mL of isooctane was added. The solvent was evaporated at 100 °C until only the 2 mL of isooctane remained, and 10 mL of isooctane was added.

Samples were injected by a Hewlett-Packard Model 7672A automatic sampler and analyzed with a Hewlett-Packard Model 5840A gas chromatograph equipped with an electron-capture detector and a capillary inlet system fitted with a fused silica capillary column (HP, 12.5 m × 0.25 mm (i.d.), coated with methyl silicone). Gas chromatography conditions follow: injection volume, 2 μL; injection mode, splitless for 1 min; carrier gas, hydrogen; column pressure, 30 psig; carrier gas flow at 80 °C, ~3 cm^3/min; split vent flow, 50 cm^3/min; makeup gas, 5% methane–95% argon; makeup gas flow, 40 cm^3/min; injection port temperature, 220 °C; detector temperature, 300 °C; initial oven temperature, 80 °C for 1 min; temperature 2, 145 °C ramped at 30 °C/min, maintained until run time 9.50 min; temperature 3, 160 °C ramped at 30 °C/min, maintained until run time 13.00 min; temperature 4, 180 °C ramped at 30 °C/min. The retention times of herbicides (derivatized compounds) were as follows: 2,4-D, 5.5 min; triclopyr, 6.5 min; 2,4,5-T, 8.5 min; picloram, 11.5 min.

Peaks were integrated automatically. Recovery was calculated by comparing observed 2,4,5-T levels with known amounts in the internal standard. The observed values for unknowns were corrected proportionally. Recovery rate in gill cups was 98%, with the standard error ±2.2%.

Foliage and litter samples were subjected to the same general procedures as the gill cups, plus a set of cleanup procedures. Dry ice was added to bulked foliage samples, which were kept frozen during processing. Each sample was chopped in a Hobart food chopper previously rinsed with acetone and 0.1 N sodium hydroxide and then cooled with dry ice. Chopping was continued until particle size was roughly 1 cm. The chopped samples were tumbled 1 min, and 10-g subsamples (±0.01) were transferred to 286-mL bottles, where they were fortified with 2,4,5-T as previously described. The contents of each bottle were transferred to a Sorval Omni-mixer (Type OM) with 50 mL of 0.1 N NaOH and ground for 30 s. Ground samples were returned to the 286-mL bottles with 200 mL of the 0.1 N sodium hydroxide rinse. The bottles were shaken for 30 min at 180 cycles/min.

A 10-mL aliquot of each sample was transferred to a vial, and 1 mL of 6 N sulfuric acid, 7 g of sodium chloride, and 20 mL of 3/7 ether/hexane were added. The vial was capped, shaken

Table I. Deposition and Variation in Gill Cups Affixed in Tanoak Crowns of Herbicides Applied by Helicopter in a Coarse Spray in Southwest Oregon

herbicide	nominal rate, kg/ha	replication	deposit/ cup, μg	coeff of variation, %	deposits/plot, kg/ha (±95% CI)	av deposit by treatment, kg/ha (±SE)	% on target
2,4-D ester	3.3	1	3028	41	4.76 ± 0.87		
		2	1419	37	2.23 ± 0.37	3.80 (±0.79)	115
		3	2808	29	4.41 ± 0.56		
	2.2	1	1442	61	2.26 ± 0.61		
		2	481	79	0.76 ± 0.27	1.35 (±0.46)	61
		3	647	43	1.02 ± 0.20		
picloram salt	0.6	1	146	104	0.23 ± 0.11		
		2	323	97	0.50 ± 0.22	0.65 (±0.29)	108
		3	767	102	1.21 ± 0.55		
triclopyr amine	4.4	1	1554	61	2.44 ± 0.66		
		2	2365	62	3.72 ± 1.03	3.12 (±0.37)	71
		3	2035	62	3.20 ± 0.89		
	2.2	1	1359	38	2.14 ± 0.36		
		2	701	57	1.10 ± 0.28	1.59 (±0.30)	72
		3	968	45	1.52 ± 0.31		
triclopyr ester	3.3	1	2329	81	3.66 ± 1.32		
		2	1608	54	2.53 ± 0.61	2.64 (±0.55)	80
		3	1098	37	1.73 ± 0.29		
	1.65	1	809	60	1.27 ± 0.34		
		2	696	83	1.09 ± 0.40	1.21 (±0.06)	73
		3	809	84	1.27 ± 0.48		

5 min at 280 cycles/min, and centrifuged 30 min at 2000 rpm. The organic layer was transferred to another vial to which 15 mL of 0.1 N sodium bicarbonate was added, shaken 5 min, and then centrifuged 1–2 min at 2000 rpm. Extraction of the aqueous phase was repeated with an additional 20 mL of ether/hexane and subsequently with 10 mL of diethyl ether. Organic phases were discarded, and 4–6 g of sodium chloride was added to the remaining aqueous phase. One milliliter of 6 N sulfuric acid was slowly swirled into the solution, which was left to stand until carbon dioxide no longer evolved. This solution was similarly extracted twice with 10-mL aliquots of ether. Organic phases were evaporated to about 2 mL at 50 °C with dry nitrogen. Each sample was then methylated with 0.25–0.50 mL of a solution of diazomethane in ether (18 mg/mL), swirled, and evaporated to about 1 mL for cleanup.

Alumina microcolumns were prepared for cleanup by placing a loose glass wool plug in 15-cm Pasteur pipets and adding 2.0–2.5 cm of 4% water-deactivated acidic alumina to each pipet. Each column was then washed with 1.5 mL of diethyl ether and the eluent discarded. Vials were placed under each column and samples transferred to the columns by Pasteur pipets, followed by a 5-mL ether rinse. The transfer and rinse were repeated twice, and the column was finally eluted with an additional 1.0 mL of ether. A 2-mL portion of isooctane was added to each vial and then evaporated at 100 °C until only the isooctane refluxed down the sides of the vial. An additional 8 mL of isooctane was added to each vial, at which time samples were ready to inject into the gas chromatograph. Chromatographic analysis conditions were the same for foliage and litter samples as for the gill cup samples. Recovery rates for foliage and litter samples were 81 and 66%, respectively, with the standard error ±1.1%, based on the internal standard. Standard errors in recovery varied by compound, 2,4-D having 0.8%, triclopyr 0.9%, and picloram 4%.

Soil residues were extracted by adding 200 mL of 0.4 M sodium hydroxide in 80% methanol to 50 g of soil in a centrifuge bottle. After the bottle was heated 30 min in a steam bath, the sample was centrifuged and the supernatant removed. The extraction was repeated with 100 mL of extracting solution, and the combined extracts were concentrated to about 150 mL on a rotary evaporator. The extract was diluted with 400 mL of water containing 10 g of sodium chloride and acidified with 20 mL of 6 N sulfuric acid. Residues of the triclopyr were extracted with two successive 120-mL portions of benzene.

The combined benzene extracts were evaporated to dryness in a 50-mL screw-cap volumetric flask and methylated by adding 5 mL of 10% BF_3 in methanol and then heating the sealed flask in a steam bath 1 h. After cooling, the excess BF_3 reagent was destroyed by adding 45 mL of water. Methyl triclopyr was extracted with two 70-mL portions of benzene, and the combined extracts were evaporated to 10 mL on a steam bath. The benzene extract was purified by passage through a 7-g column of basic alumina. The effluent and 5-mL benzene wash were evaporated to 10 mL in preparation for gas chromatographic analysis, which was performed on a Varian 200 gas chromatograph equipped with an electron-capture detector. The glass column was 2 × 2 mm and was packed with 5% OV-225 on Gas Chrom Q. Column temperature was 185 °C. Determinations were converted to milligrams per kilogram (ae), dry-weight basis.

Statistical Procedures. Deposition rates calculated from individual gill cup residues were converted to an area basis (sample size 60). Reliability of estimates was evaluated with 95% confidence limits about the means for each herbicide rate and replication. Mean concentrations (±95% confidence limits) in crown and browse foliage and litter were calculated for each herbicide, with the whole plots as sampling units (sample size 3). Mean plot concentrations and gill cup deposits were regressed against the nominal application rate to determine the generalized pattern of concentration in each stratum as a function of application rate.

Exponential decay curves were applied to residue data for each treatment and each site. Estimated values of half-life within treatments varied so much that it became obvious that first-order decay fitting is inappropriate in this set of environments. We therefore limited analyses to estimation of 95% confidence limits for each herbicide in each part of the ecosystem on each date. Because the range of environment includes upper and lower temperature and moisture conditions for much of the sclerophyll brush region, these confidence limits will include the range of expected values in most similar environments.

RESULTS

Initial Deposits. Overall rate of herbicide deposition in the gill cups was about 83% (±5.86%, 95% confidence limits) of the nominal application rate according to the relation

$$\text{CUPDEP} = 0.0018 + 0.8123\text{NOMRAT} \quad (2)$$

$$r^2 = 0.57, P < 0.01$$

where CUPDEP = herbicide deposit in the Gill cups, and NOMRAT = nominal application rate of herbicide loaded into the aircraft, both in kilograms per hectare. The lower application rates tended to have higher coefficients of variation of deposition than the higher application rates, even though application volume was constant in all treat-

Table II. Herbicide Concentrations Observed ± 95% Confidence Limits (and Predicted) in Tanoak Foliage and Underlying Litter Sprayed by Helicopter at Various Rates in Southwest Oregon

nominal rate, kg/ha	herbicide concentration, mg/kg, fresh-weight basis		
	crown foliage	browse foliage	litter
0.60	22 ± 2 (24)	11 ± 4 (24)	55 ± 66 (58)
1.65	68 ± 26 (74)	37 ± 10 (33)	55 ± 47 (69)
2.20	142 ± 60 (100)	76 ± 39 (38)	53 ± 26 (74)
3.30	142 ± 30 (153)	47 ± 16 (48)	60 ± 29 (86)
4.40	221 ± 147 (206)	48 ± 17 (57)	19 ± 19 (97)

ments. Such variation reduces the r^2 value for eq 1 but helps to meet the assumptions of regression. Differences in deposition of ester and salt formulations were negligible when expressed as percentages of the nominal rate, as shown—with deposition rates of individual replications—in Table I.

Gill cups outside plot boundaries occasionally received detectable amounts (up to 1% of the nominal rate) of herbicide. One cup, <1 m outside and downwind of a sprayed plot, received an amount very close to the nominal rate. No deposits were measurable more than 50 m from a plot boundary. Occasionally, we detected deposits from one sprayed plot in the sample grid of a neighboring plot. Again, rates were seldom more than 1% of the nominal rate in the neighboring plot when 30 m from the source plot boundary.

Herbicide deposits in tanoak crown foliage did not correlate closely with those in the gill cups. Only 42% of the variation in crown foliage deposit was accounted for by the nominal application rate

$$\text{CFOL} = -6.32 + 48.37\text{NOMRAT} \quad (3)$$

$$r^2 = 0.423, P < 0.01$$

where CFOL = deposition rate in crown foliage, in milligrams of herbicide per kilogram of foliage (fresh-weight basis).

Correlation between the milligrams of herbicide per kilogram of fresh tanoak browse foliage (BROFOL) and the nominal rate was not significant

$$\text{BROFOL} = 18.65 + 8.82\text{NOMRAT} \quad (4)$$

$$r^2 = 0.126, P > 0.10$$

nor was correlation between deposit in litter and the nominal rate ($r^2 = 0.016$, $P > 0.10$).

Deposit in browse foliage was significantly but weakly correlated with that in crown foliage:

$$\text{BROFOL} = 20.9 + 0.173\text{CFOL} \quad (5)$$

$$r^2 = 0.27, P \leq 0.05$$

Equations 3–5 were fit to the data, and herbicide deposits in tanoak foliage and underlying litter were predicted for each nominal application rate (Table II) to illustrate the hazards of predicting individual conditions from a general set of deposition data. On the basis of fresh-weight samples (39–49% moisture content), herbicide concentrations would increase 64–96% in dry-weight samples of foliage and 10–25% in dry-weight samples of litter.

Above-Ground Residues. Initial herbicide concentrations in crown foliage averaged 44 mg/kg for each kilogram per hectare applied (Table III). The sampling error of 4.3 mg/kg demonstrates that this is a generally useful value for predicting the herbicide in the top layer of tanoak or similar foliage. Concentrations in the browse layer (17 ± 1.5 mg/kg) were slightly more than one-third those in crowns, with about the same predictive reliability. Concentrations in litter (32.1 ± 4.9 mg/kg) were considerably higher than those in the browse layer and lower than those in the crowns, reflecting the shallower layer of material. More variability in the foliage samples reflects the differing amounts of sheltering cover and of litter within the 0.25 m^2 sampled.

From initial deposits adjusted for rate applied (Table III), and from changes in concentration over time, we calculated half-time estimates for herbicides in crowns and in browse and litter layers (Table I) based on $y = \beta_0 - \beta_1 \ln X$, where y = milligrams per kilogram detected at time X, β_0 = initial concentration, and β_1 is the coefficient of the degradation slope. There were many instances in which first-order decay equations introduced serious bias into our interpretations. The first-order curve usually underestimated the initial rate of decay because it is forced through later points that describe a long, inactive winter period. The assumption of constant conditions for a continuous function are obviously not met; hence, our half-time estimates are useful only for comparisons among our treatments.

A general picture of comparative rates of loss show proportional decay rates for crown foliage, browse layer, and litter (Figures 4–6). The latter provides one explanation of the lack of applicability of first-order decay to any series of samples. Litter obviously picked up herbicide deposits from leaf fall during the sampling period. The leaves were largely upper foliage that had received the highest dosage. Leaves falling from twigs change the ratio of surface to mass in the remaining crown samples, and also the matrix in which decay is occurring. We do not, therefore, recommend any extension of the half-time data.

Soil Residues. Soil pit locations with no intercepting cover and negligible shrub litter (herb litter only) received a full nominal surface loading of herbicide before the pits were dug. The soil analyses thus represent maximum levels of contamination, much higher than would be expected under the prevailing forest canopy (Newton et al., 1984). Pits were close enough to treated vegetation, however, that wind blew small amounts of litter fall from treated bushes on or near them.

Data from the surface layer on day 37 (Table IV) is presumed to represent the entire profile residue because there had been no rainfall to move it downward. It is notable that the proportion of total residue in the lower depth zone increased with time after application, presumably reflecting continuing low rates of downward movement. Relatively little change in proportions occurred with the extreme leaching pressure of winter rains. Picloram did not move downward in detectable amounts. Even allowing for the lower rate of application relative to 2,4-D and triclopyr, the amount of residue expected at depths greater than 15 cm (0.05 mg/kg) would have been well within detection limits.

All herbicide concentrations in the surface layer decreased rapidly initially and then more slowly through the winter months. The first rains caused residues of 2,4-D and triclopyr to move downward before substantial adsorption occurred, and the residues that moved quickly into deeper layers changed slowly, apparently in place, after day 79. Subsequent movement was more limited, seldom causing lower levels to exceed concentrations near the surface.

Concentrations seldom reached more than 0.020 mg/kg in the bottom layer. Between January and July (153–

Table III. Initial Concentrations of Herbicide in Crowns, Browse Layer, and Litter, Concentrations Adjusted for Application Rate, and Calculated Half-Times (Days)

herbicide	applicn rate, kg/ha	sample type	init concn (±95% CI), mg/kg	adjusted concn, mg/kg per kg/ha appl	estd half-times,[a] days
2,4-D	3.3	crown	157 ± 67	47.6	234.7
		browse	58 ± 12	17.6	36.9
		litter	66 ± 55	20.0	127.0
2,4-D	2.2	crown	66 ± 4	30.0	57.6
		browse	26 ± 2	11.8	38.8
		litter	74 ± 55	33.6	18.9
picloram	0.6	crown	22 ± 2	36.6	32.9
		browse	11 ± 4	18.3	23.2
		litter	55 ± 66	86.7	26.0
triclopyr ester	1.65	crown	68 ± 26	41.2	127.3
		browse	37 ± 10	15.2	290.9
		litter	55 ± 47	33.3	31.1
triclopyr ester	3.3	crown	127 ± 56	38.5	73.5
		browse	37 ± 28	11.2	202.3
		litter	53 ± 26	24.1	31.0
triclopyr amine	2.2	crown	142 ± 60	64.5	18.9
		browse	76 ± 39	34.5	21.4
		litter	53 ± 26	24.1	31.0
triclopyr amine	4.4	crown	221 ± 147	50.2	29.0
		browse	48 ± 17	10.9	56.0
		litter	19 ± 19	4.3	54.1
		mg/kg av in crowns per kg/ha applied = 44 ± 8.6, 95% CI			
		browse		17.1 ± 3.1	
		litter		32.1 ± 9.8	

[a] Half-time estimates for litter have little meaning because litter falling on the ground compensates loss. If this is a valid model, values given are thus substantial overestimates of actual half-time.

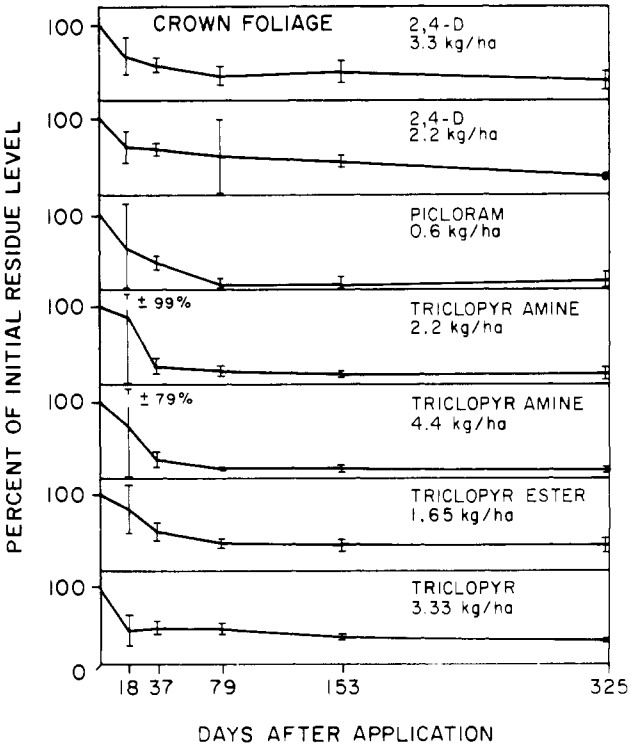

Figure 4. Percentage of initial residues remaining on crown foliage for 325 days following treatment (95% confidence intervals).

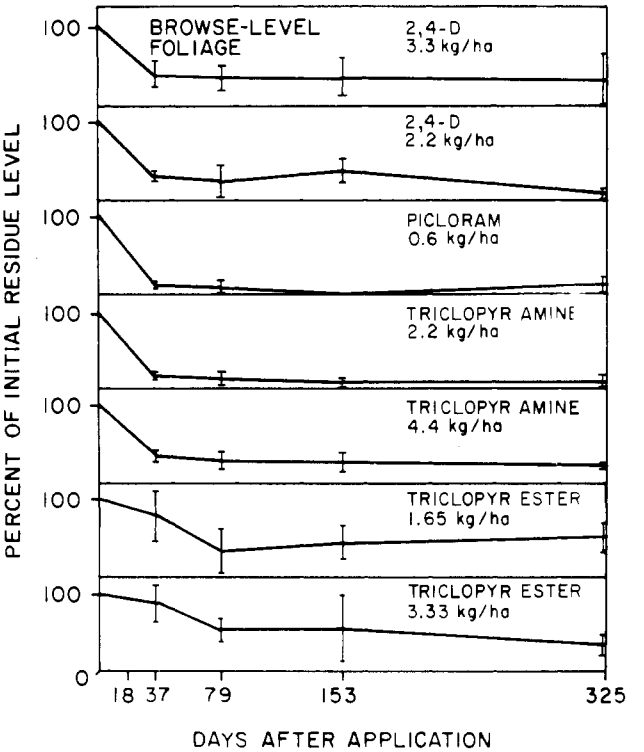

Figure 5. Percentage of initial residues remaining on browse-level foliage for 325 days following treatment (95% confidence intervals).

325 days after treatment), changes were imperceptable at that depth. Input and dissipation were almost equal; there was apparently little input, and conditions for degradation would have been poor because of low organic matter and the generally poor substrate for microbial activity. Precipitation was heavy in the first half of this interval, and most residues had probably been adsorbed and deactivated. However, temperature and moisture conditions were favorable for microbial activity in April, May, and June, which suggests that residues were bound in a nonaccessible form.

None of the soil samples showed that herbicide from an adjacent up-slope treatment had moved along bedrock in subsurface moisture, although the samples from the deepest layer came from bedrock depth or very near it. This may be evidence that movement by subsurface flow is negligible, regardless of the herbicide used. The heavy winter rains on shallow soil and steep terrain gave maximum opportunity for such movement.

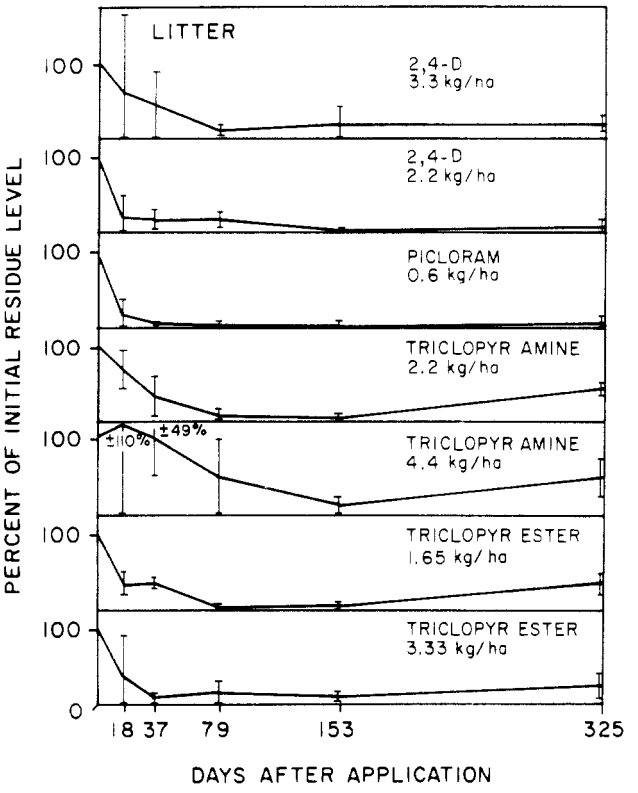

Figure 6. Percentage of initial residues remaining on litter for 325 days following treatment (95% confidence intervals).

Absolute rates of herbicide degradation are not the same as observed rates, which are concentrations reflecting input less output minus degradation. Concentrations decreased rapidly in all surface samples. Parts of the residues of 2,4-D and triclopyr were carried from surface soil into lower layers, decreasing residues in the surface, which was initially the only reservoir. There was negligible migration of picloram to deeper levels, so degradation at the surface must have accounted for nearly all loss, most of which occurred under dry conditions. A small amount of the other herbicides may have leached out of the sample area. If depth × concentration is calculated for total residues (including values for the 15 cm between the second and third sample layers approximating the average concentrations of layers above and below), one can estimate the total amount of herbicide remaining in the soil. Average concentrations from the whole profile may be used to determine whether total residues decline and, if they do, at what rates (Table V).

Soil profile residues adjusted for bulk density and depth ranged initially from 0.36 to 1.14 kg/ha. Judging from the herbicide that was observed to land on target, 30–53% of the 2,4-D, 55% of the picloram, and 24–51% of the triclopyr deposits were still present in or on dry surface soil 37 days after application. Soils were nearly bone dry through day 37. Loss during that dry period is consistent enough to suggest some mechanism of disappearance other than microbial degradation. The same ratios of amine and ester forms entered the soil, indicating that volatility of esters had little influence on loss or that two processes removed the two formulations at the same rates under hot, dry conditions.

About 90% of all herbicides had disappeared from the soil by day 325 after treatment. Picloram had a more rapid rate of disappearance, overall, than the other herbicides. With all rates and formulations of 2,4-D and triclopyr, the largest decrease in soil occurred from 37 to 79 days after treatment (the warm, moist period), the half-life ranging from 11 to 25 days during that period. Little degradation or migration out of the profile occurred between the next two sample dates despite the large movement of water through the profile. In the spring, further losses occurred, presumably as the result of increased soil temperatures and activation of the microbial community. In the absence of studies of metabolites, we must regard this as circumstantial evidence that dissipation is through microbial activity.

DISCUSSION

Deposition. The large number of observations gives assurance that 78–88% of the applied herbicide, or more, landed in the project zone. Disorientation of gill cups by rotor wash probably slightly reduced the capture of drops, and the actual targeting was probably in the upper end of this range.

The high coefficient of variation in the gill cup readings is notable. In calibration runs with the helicopter, we observed a degree of blotchiness in the pattern and occasional very large drops ("bombs") with estimated diameters of 2 mm or more, a volume nearly 17 times as great as that of the median drop. The variability was great enough that an appreciable percentage of small plants would receive a sublethal dose—and indeed this was observed. The large drops were also wasteful. Richardson (1989) found 250-μm drops significantly more efficient than 800-μm drops in observations of two herbicides and two forest species. Small drops were more completely intercepted, and coverage was improved.

For deposition research, catch samplers were needed in large numbers. Our use of 480 gill cups (8 treatments × 60 cups/treatment) gives a good estimate for overall helicopter targeting, but 60 cups per treatment, with an average 60% coefficient of variation, gives a standard error averaging 7.7% for individual treatments, or a 95% confidence interval of ±15%. The variability in the coefficient of variation (Table I) is an indication that local conditions influence patterns of deposition. In these applications, the highest variability occurred where the aircraft followed the contour of a steep side slope, or flew up or down a steep gradient.

The high proportion of deposits intercepted by crown foliage is in agreement with Rafferty et al. (1981). This interception protected lower foliage from lethal deposits; it also reduced contamination of wildlife forage. Yet failure to treat lower foliage effectively would lead to need for a second treatment, unless an herbicide is absorbed and translocated better than these were.

Variability in deposition of spray does not explain the variability observed in the ratio of 2,4-D to picloram in the one mixed formulation. The nominal ratio was 3.67/1, but the ratios appearing in gill cups in the three replications were 0.84, 1.49, and 9.88. The 95% confidence limits of these observations in Table I suggest that field variation and analytical procedures do not explain this anomaly. Moreover, the samples were all taken in the middle one-third of the load, removing the possibility of unmixed products at the bottom or top of the load. Although this study alerted us to the uncertainties of delivery systems, knowledge of what was actually delivered permitted us to continue the dissipation experiment without difficulty.

Behavior of the Herbicides. Some of our observations confirm behavior described elsewhere, and some suggest marked departures. Perhaps the most notable agreement is that herbicides tend to be immobile or move only short distances in a forest ecosystem from which there

Table IV. Average Concentrations of Herbicide in Three Soil Depths, by Number of Days after Treatment[a]

herbicide	applicn rate, kg/ha	depth, cm	residue (±95% CI), mg/kg 37 days	79 days	153 days	325 days
2,4-D	3.3	0–15	0.76 ± 0.88	0.109 ± 0.190	0.076 ± 0.070	0.021 ± 0.010
		15–30		0.030 ± 0.020	0.017 ± 0.004	0.009 ± 0.008
		45–60		0.008 ± 0.002	0.014 ± 0.012	0.014 ± 0.019
2,4-D	2.2	0–15	0.475 ± 0.63	0.038 ± 0.014	0.028 ± 0.016	0.020 ± 0.010
		15–30		0.013 ± 0.007	0.023 ± 0.011	0.015 ± 0.007
		45–60		0.007 ± 0.009	0.016 ± 0.010	0.017 ± 0.020
picloram	0.6	0–15	0.242 ± 0.276	0.043 ± 0.048	0.009 ± 0.008	ND
		15–30		ND	ND	ND
		45–60		ND	ND	ND
triclopyr amine	2.2	0–15	0.256 ± 0.222	0.141 ± 0.150	0.064 ± 0.053	0.016 ± 0.019
		15–30		0.030 ± 0.039	0.021 ± 0.022	0.007 ± 0.002
		45–60[b]		0.012 ± 0.017	0.009 ± 0.011	0.008 ± 0.007
triclopyr amine	4.4	0–15	0.690 ± 0.365	0.207 ± 0.163	0.117 ± 0.098	0.019 ± 0.007
		15–30		0.033 ± 0.027	0.021 ± 0.006	ND
		45–60[b]		0.010 ± 0.003	0.008 ± 0.003	ND
triclopyr ester	1.65	0–15	0.453 ± 0.098	0.086 ± 0.071	0.045 ± 0.034	0.020 ± 0.024
		15–30		<0.005	0.012 ± 0.002	0.005 ± 0.005
		45–60		0.005 ± 0.003	0.011 ± 0.009	ND
triclopyr ester	3.3	0–15	0.731 ± 0.115	0.017 ± 0.010	0.020 ± 0.022	0.018 ± 0.022
		15–30		ND	0.016 ± 0.022	0.009 ± 0.010
		45–60		0.005 ± 0.005	0.036 ± 0.061[c]	0.028 ± 0.051[c]

[a] ND = not detected at <0.005 mg/kg detection limit. [b] Because of shallow soils, deepest samples were at 30–45 cm in one of six pits for the 2.2 kg/ha triclopyr amine treatment and in two of six pits for the 4.4 kg/hg treatment. [c] Large sampling error, possibly attributable to contamination. The unusually high value occurred where both other determinations were below the detection limit of <0.005 mg/kg.

Table V. Integrated Concentrations of 2,4-D, Picloram, and Triclopyr in the Top 60 cm of Soil, by Number of Days after Treatment

herbicide	applican rate, kg/ha	average concentration (±95% CI), mg/kg 37 days	79 days	153 days	325 days
2,4-D ester	3.3	0.190 ± 0.220	0.041 ± 0.041	0.030 ± 0.019	0.014 ± 0.008
2,4-D ester	2.2	0.119 ± 0.157	0.017 ± 0.006	0.021 ± 0.007	0.017 ± 0.007
picloram, K salt	0.6	0.060 ± 0.069	0.011 ± 0.012	<0.005[a]	ND[b]
triclopyr amine	2.2	0.064 ± 0.055	0.051 ± 0.040	0.027 ± 0.017	0.010 ± 0.005
triclopyr amine	4.4	0.172 ± 0.091	0.068 ± 0.037	0.040 ± 0.021	0.005 ± 0.002
triclopyr ester	1.65	0.114 ± 0.025	0.023 ± 0.028	0.020 ± 0.009	0.007 ± 0.008
triclopyr ester	3.3	0.183 ± 0.279	0.017 ± 0.004	0.024 ± 0.020	0.018 ± 0.016

[a] One of three samples was at the detection limit of 0.005; others were below the limit. [b] None detected at limit of detection, 0.005.

is negligible surface runoff. We found no evidence that large amounts of herbicide moved to 60-cm depth in the soil but considerable evidence that herbicide tied up in vegetation is not readily removed until the vegetation becomes litter.

Norris's review (1981) of phenoxy herbicides indicates that the distances they move in soil are small compared to the distances necessary for transport to streams. Blackman et al. (1974) observed that 2,4-D, 2,4,5-T, and picloram were distributed in wet tropical forests much as 2,4-D and triclopyr were distributed in this study. Their reports showed more downward mobility of picloram in warm, wet conditions than we observed with comparable or less moisture in colder soil. The half-times of 2,4-D and triclopyr that we observed in warm soil are within ranges noted in the literature on soil degradation for 2,4-D and 2,4,5-T. Norris (1981) noted that in many studies 2,4,5-T degraded more slowly than 2,4-D. Our data suggest that triclopyr, structurally similar to 2,4,5-T, is more like 2,4-D in movement and persistence.

Plumb et al. (1977) reported on the persistence of phenoxy herbicide in a hot, dry California brushfield in a situation approximating that of our study except for quantity of moisture. They monitored residues in soils for more than 1 year, observing that the half-time was about 19 days. Their report does not give conditions immediately after treatment, but they found an early rapid breakdown followed by decreasing rates of loss. The initial rapid loss from surface soil was similar to our finding, and the slow loss from all layers resembled ours 2 months or more after application. Residues throughout the profiles they examined indicate that rainfall occurred between herbicide application and the first observation; hence, they had little opportunity to observe surface degradation. They did not estimate total residue in all soil depths. Nevertheless, the similarity of their data to ours suggests that residues may decline relatively rapidly in moist warm soil, but that losses are probably slow at other times (e.g., in cold, dry soil). Data from our study suggest further that loss of deposits on dry surface soil is almost as great as loss in moist surface soil and that residues are tied up sufficiently in soil to prevent substantial leaching. In particular, data from one steep site with 3500 mm of precipitation provide strong evidence for downslope immobility of all such residues.

Picloram degraded similarly to 2,4-D and triclopyr before rains and dissipated as fast or faster after movement into the soil. After onset of rains, it was less mobile than 2,4-D or triclopyr. Goring and Hamaker (1971) described the behavior of picloram in a leaching and degrading soil profile as a rising and subsiding wave. We observed a similar weak pattern in lower soil depths with 2,4-D and triclopyr, but picloram did not move below the surface layer. As the tendency elsewhere is for picloram to be more mobile and more persistent than phenoxy herbicides (Norris, 1970; Helling, 1971), we regard this to be a significant departure from most evidence about picloram persistence. The total absence of detectable picloram below 15 cm under a range of leaching conditions suggests that there is no measurement error. The three

sites were sufficiently different in soils and rainfall to suggest that our observation is tied to features of the soil, such as high clay content, aggregation, and infiltration rate.

The rate of disappearance of picloram in soil in this study is comparable to that reported for an array of other herbicides (Hay et al., 1974)—either shorter or about equal to the shortest half-time reported. Merkle et al. (1973) found decomposition rate more dependent on soil temperature and moisture content than on soil type or original concentration. Our data suggest that conditions in the Siskiyou Mountains are most favorable for rapid disappearance during early fall. The rapid breakdown before entry into the soil suggests that physical processes complement microbial degradation in the disappearance process and that conditions are favorable for both.

Losses of herbicide from foliage and litter were less well-defined than those in soil. In general, all herbicide residues decreased quickly after application, leveled off 79 days after treatment, and then began a period of slow loss that continued until the following summer. Picloram was the exception; little remained at day 79 despite negligible rainfall or dew. Presumably, the same mechanism destroyed picoloram on foliage and on soil, but it did not remove other compounds, especially those applied as esters. Norris et al. (1976), working in a nearby but drier zone, observed that picloram persisted longer than 2,4-D but that it was confined to surface soil under leaching conditions.

Radosevich and Bayer (1979) observed that triclopyr amine did not translocate readily out of tanoak leaves, which suggests that residues do not decrease significantly as the result of export to other parts of the plant, woody sinks in particular. The tendency toward photochemical degradation may be limited by herbicide absorption such that ultraviolet radiation cannot reach the residues. It was our observation that the salt formulations, especially of picloram, disappeared more rapidly than the esters during the initial 37 days. Norris et al. (1986) also observed rapid loss of triclopyr amine from foliage soon after application ($t_{1/2}$ = 3–4 days). We postulate that the salts were more poorly absorbed and hence were more accessible for photochemical destruction.

After initial deposition and early losses, herbicides in evergreen foliage and twigs showed remarkable persistence. Most of the time, foliage was either dry at temperatures suitable for microbial activity or moist enough for activity but too cold. Herbicides killed the leaves slowly; no symptoms were observable for several weeks after treatment, and wilting occurred over many months. It therefore appears that opportunities for microbial colonization and activity in herbicide degradation were limited.

Crowns and browse layers showed similar rates of loss, but browse concentrations of 2,4-D and triclopyr were only about one-third of those in crown foliage. Picloram decreased to low levels before rainfall despite shading and remained low but detectable.

The litter interface between foliage and soil showed the expected trends. After initial deposition, concentrations of all materials decreased quickly, remained low but stable through the winter, and rose slightly in the spring, in some instances, as a new supply of contaminated foliage fell from the defoliating crowns.

Mobility of herbicides in soil water appeared to be slight and to be active in a downward direction over short distances. This would effectively preclude detectable concentrations in water from subsurface flow. The sites varied considerably in amounts of percolating precipitation, yet they did not vary consistently in their rates of loss. Contamination of water by each of the chemicals under consideration has been considered by Newton and Dost (1984), and Newton and Norgren (1977) have examined 2,4-D and picloram in detail. Significant water contamination would occur only where water is directly treated or where picloram is applied so that it could move overland from treated water into water channels (Norris et al., 1976).

Behavior of the herbicides in the animal food chain can be projected. With application of 3.3 kg/ha of 2,4-D, the most toxic of these herbicides, initial concentrations would approximate 50 mg/kg in forage. An animal the size of a rabbit consuming 5% of its body weight per day would take in 3 mg/kg 2,4-D daily during the period when forage was still attractive—about $^1/_{13}$-th of the acute no-effect level for 2,4-D in diets of numerous mammal species (Newton and Dost, 1984) and less than the chronic no-effect level. It is therefore highly unlikely that any animal would be exposed to a harmful dose, and the tendency for these chemicals to be eliminated quickly precludes the problem of food chain accumulation and magnification.

With identical rates of application with glyphosate, Newton et al. (1984) observed that small mammals received lower exposure than expected from forage residues. Similarly, Newton and Norris (1968) observed that deer feeding in areas treated with 2,4,5-T or atrazine had less herbicide in their rumens than expected and negligible retention in other body organs.

Picloram and, to some degree, triclopyr have some ability to damage plants via root uptake. Soil residues that could limit growth of crop trees must be avoided if the herbicides are to have successful use in forestry. In a study of triclopyr and picloram residues, Newton and Kelpsas (1989) observed that conifers do not seem to take up triclopyr from roots. Ponderosa pine (*Pinus ponderosa*) and grand fir (*Abies grandis*) were not injured by picloram residues greater than those observed here. Douglas-fir absorbed residual picloram and was slightly injured by soil concentrations greater than 0.020 mg/kg and severely injured by concentrations greater than 0.040 mg/kg. Our data suggest that application several months before planting will not result in injury to any of these conifers.

CONCLUSIONS

Aerially applied 2,4-D, picloram, and triclopyr leave detectable traces in evergreen brushfield ecosystems for nearly 1 year. Residues disappear most rapidly in soil and litter. Some abiotic losses other than volatilization probably occur between application and the first rainfall. Evergreen foliage is retained long after being damaged by the herbicides, during which time above-ground residues dissipate slowly but are retained against leaching or microbial attack so that they are not likely available to any organisms except those that feed on dry foliage. When the foliage becomes litter, herbicide degradation occurs quickly under favorable conditions. All herbicides showed little mobility in soil and rapid early dissipation. Persistent residues were immobile and apparently difficult to dislodge. The retention of residues in place suggests that their movement in water either into the soil from aerial foliage or out of the soil by leaching is unlikely. Soil residues were too low to be of concern for their effect on desirable plant species; but as there are large variations within swaths in aerial applications, spot samples for residue or deposit analysis should num-

ber 200 or more to ensure a sampling error of 10% or less in case further study is needed.

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