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Dissipation and Offsite Movement of Forestry Herbicides in Plants of Importance to Native Americans in California National Forests

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California Indians continue the tradition of gathering of plant materials for food, medicine, and for ceremonial, or basketry uses (Goode 1992). They are concerned about health risks associated with this traditional gathering, processing, and consuming of plant materials because of the potential exposure to herbicide residues from materials inadvertently gathered in or near herbicide treated areas of the National Forests.

The United States Forest Service may apply herbicides in the National Forests for reforestation activities. Glyphosate, triclopyr, and hexazinone are herbicides commonly applied before planting or in newly established conifer plantations to control competitive weeds (DiTomaso et al. 1997). This study quantifies dissipation and off-site movement of forestry herbicides on resident plants. This information will be used to determine if California Indians gathering and processing plant materials from inside and outside herbicide treatment areas are at risk from pesticide exposure.

MATERIALS AND METHODS

Using the plant selection, sampling, and analytical methodology established in Segawa et al. (1997), the dissipation and offsite movement of glyphosate, triclopyr, and hexazinone were monitored in bracken fern roots, buckbrush shoots, golden fleece foliage, and manzanita berries. This study was conducted over a four-year period (1997-2001) in Eldorado, Sierra, and Stanislaus National Forests. Herbicide applications were made by commercial pesticide applicators under contract with the US Forest Service. The four herbicide products and range of use rates were glyphosate (Accord®, 0.4-5.4 kg a.i./ha); triclopyr (Garlon® 4, 0.3-2.0 kg a.i./ha), liquid hexazinone (Velpar® L, 1.7-3.3 kg a.i./ha) and granular hexazinone (Pronone® 10G, 3). Granular hexazinone was applied by helicopter. The remaining herbicides were applied by ground crews with backpack sprayers spot treating targeted plants.

Four plant species of interest to California Indian gatherers were selected based on their cultural importance to the tribes and availability in the treatment areas. These plants represent one root-type plant (bracken fern rhizomes), one brush-

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type plant (buckbrush shoots), one foliage-type plant (golden fleece), and one food-type plant (manzanita berries) (Table 1).

Table 1. Plants selected by California Tribes for monitoring.

Common Name	Scientific Name	Plant Part Sampled	Tribal Use
Bracken Fern	*Pteridium aquilinum var. pubescens*	Roots (rhizomes)	Basketry
Buckbrush	*Ceanothus cuneatus*	Shoots	Basketry
Golden Fleece	*Ericameria*	Foliage	Medicinal
Manzanita	*Arctostaphylos spp.*	Berries	Food Source

Herbicide dissipation was monitored at 53 sites in the three National Forests. Sites were selected based on accessibility and the availability of adequate amount of appropriate plants growing in the herbicide treatment areas. Selected manzanita berry sites had flowers or berries present at the time of herbicide application. Monitoring sites were 0.8 to 108 ha in size and at elevations ranging from approximately 750 to 1,800 m. Conditions differed between sites including the month of herbicide application, climatic conditions, and stage of plant maturity.

Six to 20 buckbrush, golden fleece or manzanita plants at each monitoring site were tagged with flagging tape for sampling. Bracken fern was generally pervasive, so a 3 to 6-m diameter circle was marked off with stakes so that root samples would be collected within this enclosed region. Plant samples were collected at seven intervals: within 1-3 days, and within 3-5, 7-9, 11-13, 19-21, 27-29, and 35-37 wk following herbicide application. Additional sampling were taken beyond 37 wk at 11 sites showing the highest residue concentration for each plant part/herbicide product combination reported at sampling week 35-37. Monitoring was later discontinued at these high residue sites due to lack of further herbicide detections, inaccessible roads due to snow or heavy rains or inadequate supply of plant materials.

Offsite movement for herbicide residues were monitored in 20 sites with bracken fern roots, buckbrush shoots, and deerbrush shoots (*Ceanothus integerrimus*). To be included, plants had to be available, adjacent and 30-m down slope to the herbicide treatment areas. Flagging tape was used to mark four distances along the 30-m transect at 1.5-4.5, 6-12, 15-21, and 24-30 m from the edge of the treatment site. Plant samples were collected at each distance to characterize herbicide movement from the edge of application area. Samples were collected at four periods: prior to herbicide application (background sample), 1-3 days post-application, and 3-5 and 11-13 wk post-herbicide application.

Roots, shoots, foliage, and berries samples were collected from pre-selected plants with green foliage that had no signs of herbicide effects (e.g., brown discolored vegetation), and later samples were collected from herbicide-affected

plants. Clean disposable latex gloves were worn to collect samples. Gloves were changed between each sample collected to reduce herbicide cross-contamination. Cleaned handheld pruning shears were used to cut buckbrush shoots, golden fleece foliage, and manzanita berries directly into a 0.9L glass jar. Leaves of the deerbrush shoots were removed with the pruning shears and discarded and the barren shoots were placed into the sample jar. A clean shovel or hand trowel was used to expose bracken fern roots, which were shaken to remove excess soil before being placed in the sample jar. Each sample consisted of approximately 0.1 kg of plant material. Sample container openings were lined with aluminum foil and then tightly sealed with a lid before being placed on dry ice and frozen until chemical analysis.

The analytical methods are described in Segawa et al. (1997). The minimum detection limit and method recovery ranges were as follows: glyphosate (0.1 ug/g, 79-94%); triclopyr (0.03-0.07 ug/g, 75-93%) and hexazinone (0.05-0.1 ug/g, 90-93%). Results from method validation studies were used to develop control charts for quality control purposes. Lower and upper warning limits (mean $\pm$ 2 SD) and control limits (mean $\pm$ 3 SD) were calculated to determine if results were within an acceptable range. Field samples were extracted along with plant parts fortified with known herbicide addition(s) and also with unfortified plant parts containing no herbicide residue. Residues of glyphosate, triclopyr, and hexazinone are presented on a fresh weight basis.

Monitoring results for each plant/chemical combination generated a generally declining time series of residual concentrations. Each curve was fitted to a negative exponential function using the Levenberg-Marquardt method. Half-lives were calculated from equations showing an acceptable degree of fit. There were four time series for each plant/chemical combination, and potentially four half-life values can be obtained. These values are screened using two criteria: the fitted equation must be significant at the 90% confidence level, and the half-life calculated from the equation must be a positive value. The half-life values passing the screening were averaged using the R^2 as the weight coefficient. This weighted average value was the half-life estimate for that specific plant/chemical combination. The number of values potentially included in an average varies from 4 to 0; the later represents an extreme case where no meaningful regression is obtained.

RESULTS AND DISCUSSION

The herbicides showed a general decline trend in concentration over time (Figure 1). Glyphosate application-day residue means ranged from 0.5 to 241 ug/g for bracken fern roots, buckbrush shoots, golden fleece foliage, and manzanita berries. Levels were approximately 2 to 900 times greater than mean application-day residue levels for the three remaining herbicide products on the same media. High levels were attributed to direct spray of glyphosate on plant material using a higher application rate than the other foliar applied herbicides. Mean glyphosate residue levels in buckbrush shoots, golden fleece foliage, and manzanita berries

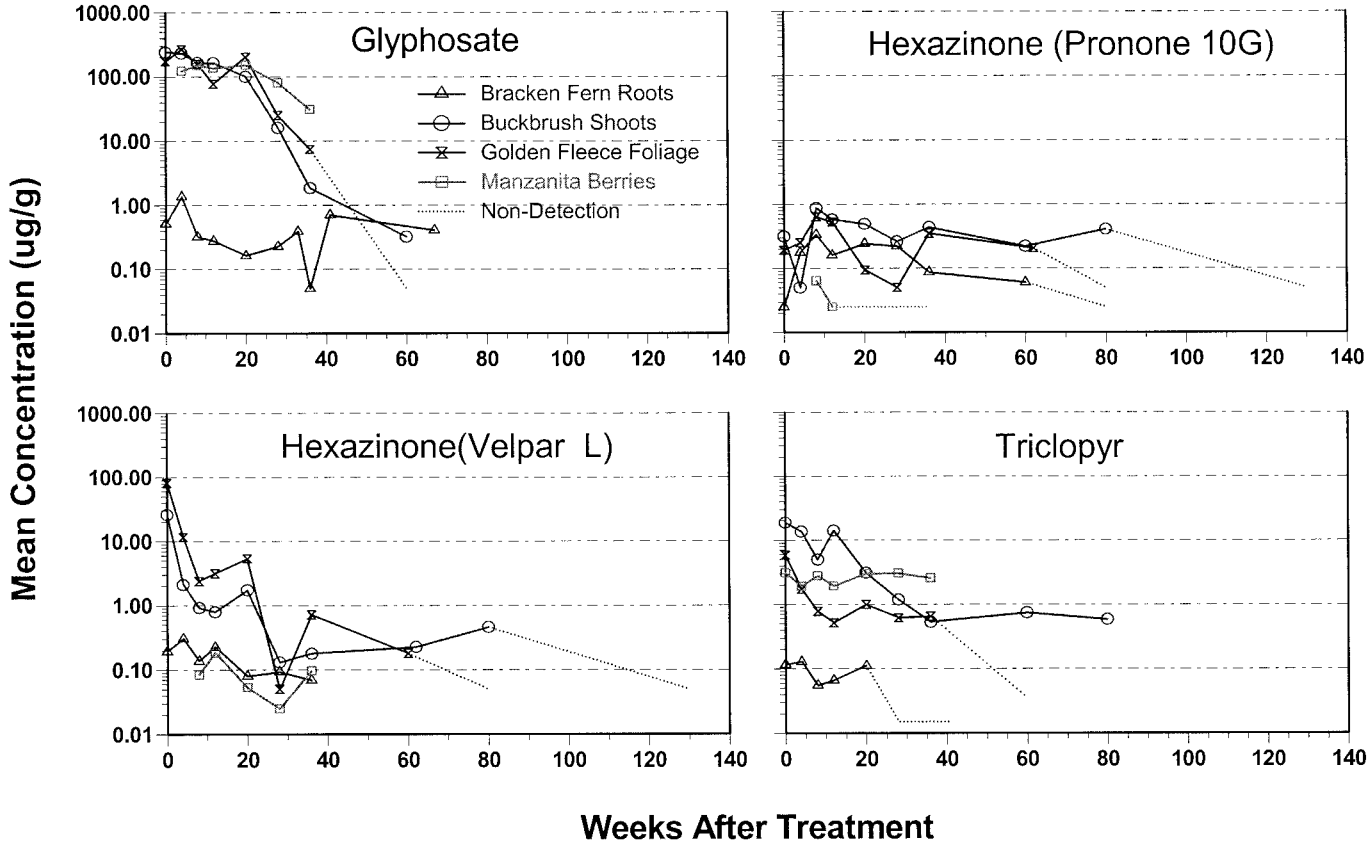

Figure 1. Dissipation of herbicide in plants, Eldorado, Sierra and Stanislaus National Forests, Calif., 1997-2001.

remained above 75 ug/g during the first 20 wk and then declined to nondetect for golden fleece and less than 1 ug/g for buckbrush by week 60, with the exception of manzanita berries, which had 31 ug/g at week 36 that berries were available for sampling. Foliar applied glyphosate was quickly translocated to the roots of bracken fern with a mean concentration of 0.5 ug/g 1-3 days following herbicide treatment. At week 67, the last sampling date for bracken fern roots, glyphosate residue remained detectable at 0.4 ug/g.

Triclopyr was detected on application day in all media sampled including bracken fern root with mean levels ranging from 0.1 to 19 ug/g. Bovey et al. (1983) also reported rapid triclopyr movement to the root system within four hours following triclopyr application to a single leaf of the honey mesquite plant (*Prosopis juliflora* var. *glandulosa*). Residues were not detected beyond the 20 wk sampling period for bracken fern roots or 36 wk in golden fleece foliage. However, triclopyr was detected in buckbrush shoots and manzanita berries throughout the monitoring period. On the last sampling date buckbrush shoot had 0.6 ug/g (week 80) and manzanita berries 2.6 ug/g (week 36).

Liquid hexazinone applications resulted in higher mean application-day residue levels in buckbrush shoots, bracken fern roots and golden fleece foliage (0.2 to 81 ug/g) compared with granular hexazinone (non-detected to 0.3 ug/g). Residues were detected in bracken fern roots sampled on application day for liquid but not granular hexazinone. Manzanita berries were not available until week 8. Granular hexazinone application-day plant samples showed the presence of hexazinone residue in buckbrush shoots (mean = 0.3 ug/g) and golden fleece foliage (mean = 0.2 ug/g). Detections may have been due to herbicide dust settling on plant material from aerial application or to actual uptake by plants following application. Feng et al. (1988) reported that any amount of moisture from rainfall, dew or condensation was enough to result in significant release of hexazinone from coated granules making it available for absorption by the plant root system. Hexazinone residues were detected in manzanita berries treated with granular hexazinone in only 1 of 5 sampling periods, compared with 4 of 5 for liquid hexazinone treated plants. Low hexazinone detections may indicate low uptake, low translocation, or rapid degradation within the plant for granular hexazinone (Sidhu and Feng 1993). Baron and Monaco (1986) reported that plant cuttings of rabbiteye blueberry (*Vaccinium Ashei* Reade) and highbush blueberry (*Vaccinium corymbosum* L.) absorbed less hexazinone from hexazinone root applications than did hollow goldenrod (*Solidago fistulosa* Miller) plant cuttings, resulting in less hexazinone translocated to the leaves of both species of blueberry plants. Maximum mean hexazinone residue levels for granular hexazinone were observed at 8 wk post-application. These levels were approximately three or more times greater than at application-day for bracken fern roots, buckbrush shoots, and golden fleece foliage. Latent high residue levels were generally not observed with foliar applied herbicides, which showed maximum residue levels in plants immediately following herbicide application. Large variation exists between the numbers of wk to reach the non-detectable level for each plant part/herbicide product ranging from 4 to 130 wk. Herbicide residues appeared more persistent

in buckbrush shoots than in the remaining three media. Residues of hexazinone in bracken fern roots dissipated in 4 and 29 wk for liquid and granular hexazinone, respectively. Golden fleece and manzanita plants treated with either the liquid or granular hexazinone, showed similar dissipation rates in foliage and berries, respectively.

Average herbicide half-lives ranged from 1 to 19 wk for the various plant part/herbicide product combinations (Table 2). Half-lives were longest for bracken fern roots relative to other plant parts sampled. Liquid hexazinone half-lives obtained in this study were longer than those observed by Michael (1990) who reported Velpar® L half-lives of less than 9 wk in dogwood (*Cornus florida* L.), blueberry (*Vaccinium* sps.), and bracken fern (*Pteridium aquilinum* L.) terminal shoots.

Table 2. Average half-life of four forestry herbicides in plant parts used by California Indians.

Herbicide	Average Half-Life (wk)			
	Bracken Fern Roots	Buckbrush Shoots	Golden Fleece Foliage	Manzanita Berries
Glyphosate	11.5	9.8	8.2	na*
Triclopyr	6.1	2.4	5.1	na
Hexazinone-Liquid	18.5	17.6	0.6	na
Hexazinone-Granule	na	na	na	1.7

*na denotes that no meaningful regression could be obtained because of high variability of the data; therefore, no average half-life was calculated.

Residues of glyphosate, triclopyr, and hexazinone were detected outside the treatment area following application to bracken fern roots, buckbrush shoots, and deerbrush shoots (Table 3). Residues ranged from none-detected to 2.7 ug/g. Of the 240 off-site samples collected, only 19 (7.9%) contained herbicide residues and approximately 33% of the detections were at or close to the detection limits. The glyphosate detected (0.1 ug/g) at two locations on the 6-12 m transect collected 12 wk post-application were most likely due to contamination since they were not detected at this distance at the earlier dates. This is probably the case also for the hexazinone detection (0.01 ug/g) reported at the 7.2-9 m distance. Rain runoff was likely the source of the 0.7-ug/g hexazinone detection at 12-wk post-application of liquid hexazinone. Prominent gullies crossing the road from the treatment area to the transect were observed at week 12. These gullies were not apparent prior to week 12 sampling. It is assumed that herbicide residues were transported with rainfall/snowmelt moving the 15-27 m distance and ultimately to be translocated by the sampled plants. Residues were not detected at this monitoring location in samples earlier than week 12. Hexazinone has a high potential to move off-site due to its high water solubility and low adsorption to

soil (Worthing 1979), so this detection was not considered unusual. Granular hexazinone was detected at the 1.5-4.5 and 15-21 m distances, with concentrations of 0.1-1 ug/g at 1-3 days following herbicide application. The detections were probably from herbicide dust deposition on plants.

Table 3. Off-site movement of herbicides detected in plants at various distances from treatment areas in Eldorado, Sierra and Stanislaus National Forests, Calif. 1997-2001.

Chemical	Weeks after Application	No. of detections Meters from Edge of Treatment Area			
		1.5-4.5	6-12	15-21	24-30
Glyphosate	0	3	ND*	ND	ND
	4	2	ND	ND	ND
	12	ND	2	ND	ND
Triclopyr	0	2	2	2	1
	4	ND	ND	ND	ND
	12	ND	ND	ND	ND
Hexazinone (liquid)	0	ND	ND	ND	1
	4	ND	ND	ND	ND
	12	ND	ND	1	ND
Hexazinone (granule)	0	1	ND	1	ND
	4	ND	ND	ND	ND
	12	ND	ND	ND	ND

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