Dissipation and Off-site Movement of Forestry Herbicides in Plants of Importance to California Tribes

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INTRODUCTION

The California Indians continue the tradition of gathering and using native plant resources for food, basketry, medicine, and ceremonial purposes (Hutchens 1991, Strike 1994). Tribes that live in the vicinity of U.S. National Forests are concerned about exposure to forestry herbicides during gathering, processing and consuming of these plant materials grown in or near forestry lands where herbicides may have been applied.

The U.S. National Forests of Lassen, Eldorado, Sierra, and Stanislaus used glyphosate, hexazinone, and triclopyr for brush and annual weed control to re-establish conifer plantations after timber harvest or forest fires (Di Tomaso 1997). These herbicides are applied from spring through fall using a backpack sprayer or other ground equipment, or using a helicopter to apply granular hexazinone where treatment areas were large and inaccessible by ground.

The U.S. Forest Service staff, the local tribal groups, and the Department of Pesticide Regulation jointly developed two study-objectives (1) to determine the

dissipation of glyphosate, hexazinone and triclopyr in plants; and (2) to determine off-site movement of these herbicides during applications. The study was conducted in two phases. Phase I has been completed where analytical methods were developed for thirteen selected plant species, and initial dissipation and off-site movement data were collected from Lassen, Eldorado, Sierra and Stanislaus National Forest (Segawa et al. 1997).

In this final report, we discuss the results from 1997-2000 of dissipation and off-site movement on selected plants for glyphosate, hexazinone and triclopyr applied in Eldorado, Sierra and Stanislaus National Forests.

MATERIALS AND METHODS

Field Monitoring

Herbicide treated sites in Eldorado, Sierra and Stanislaus National Forests and plants of interest and abundance were selected in consultations with the local tribal groups including the Maidu, Miwok, Mono, Washo, and Nisenan, and the staff of the U.S. Forest Service. Four herbicide/application-method combinations were selected: Pronone® 10G (granular hexazinone) applied by helicopter; Velpar®L (liquid hexazinone), Accord® (glyphosate), and Garlon® (triclopyr) applied by using backpack sprayer. Four readily available plants in the treatment areas representing various plant parts and uses by tribal groups were selected: i) bracken fern roots (*Pteridium aquilinum var. pubescens*) for basket weaving, ii) buckbrush or deerbrush shoots (*Ceanothus intergerrimus*, *Ceanothus cuneatus,* respectively) for basket weaving, iii) golden fleece foliage (*Ericameria arborescens*) for medicinal purposes; and iv) manzanita berries (*Arctostaphylos* spp.) for

food. Each sample was a composite of plant materials from one to 20 plants. Samples were collected using pruning clippers or shovel as appropriate. Disposable gloves were worn and changed between each sample. Sampling equipment was decontaminated with water and methanol after taking a sample. All samples were kept in glass jars and immediately placed on dry ice and kept frozen until analysis.

The sites and application methods monitored were (1) Stanislaus National Forest sites treated with all four herbicide/application methods; (2) Sierra National Forest sites treated with hexazinone (Velpar® L) and glyphosate (Accord®) by ground; and (3) Eldorado National Forest sites treated with glyphosate and triclopyr (Garlon®) by ground. The ranges of nominal application rates in pounds active ingredient per acre were glyphosate 1-1.5, triclopyr 1-1.5, and hexazinone 3-3.5. For dissipation monitoring, 376 samples were collected from 32 sites in the three National Forests representing the four plants and four treatment/application method combinations. For the off-site movement monitoring, 253 samples were collected from 19 sites for 20 herbicide treatments at 5-15 ft, 20-40 ft, 50-70 ft and 80-100 ft from the edges of treated areas. Samples were collected one to three days following treatment, and then again at 4 and 12 weeks following application to capture any offsite movement in rain runoff and subsequent uptake by plants.

Analytical Methods

For glyphosate analysis, plant samples were homogenized, extracted with hydrochloric acid and methylene chloride, cleaned-up through ion exchange columns and analyzed using a high pressure liquid chromatograph (HPLC) with post column reactor and

fluorescence detector. The method reporting-limit was 0.1 ppm. Spiked sample recoveries ranged from 54 to 106%.

For hexazinone analysis, the plant homogenates were extracted with acetonitrile, cleaned up through solid phase extraction column, and eluted with methanol/methylene chloride mixture. The extract was analyzed using an HPLC with ultraviolet detector. The reporting limit ranged from 0.05 to 0.1 ppm depending on plant type. Spiked sample recoveries ranged from 71 to 123%.

For triclopyr analysis, homogenized plant samples were extracted with benzene/sulfuric acid mixture, cleaned up with sodium bicarbonate solution and ethyl ether. The extract was re-acidified, extracted with methylene chloride, derivatized with diazomethane and analyzed using a gas chromatograph with an electron capture detector. The reporting limit ranged from 0.03 to 0.07 ppm, and spiked recoveries ranged from 51-108% depending on plant type.

RESULTS AND DISCUSSION

Dissipation

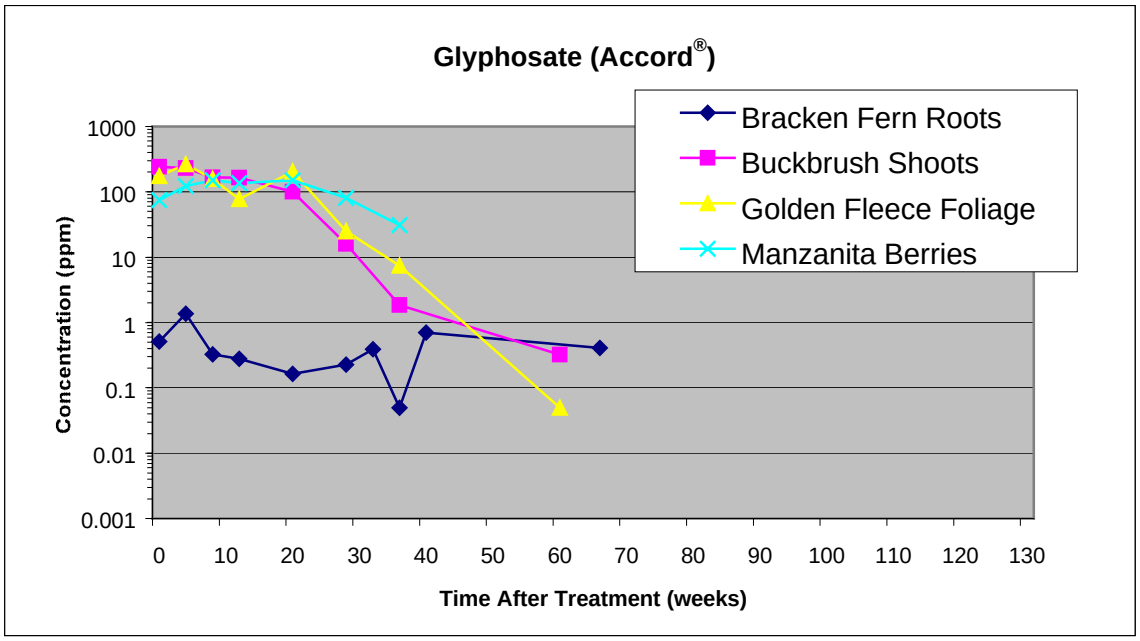
For the dissipation study, a total of 376 plant samples from 32 treatment sites were collected for 130 weeks in the Eldorado, Stanislaus and Sierra National Forests. Samples consist of the four plant species treated with one of the four chemical formulations. Figure 1 shows dissipation of each chemical formulation in the four different plant types.

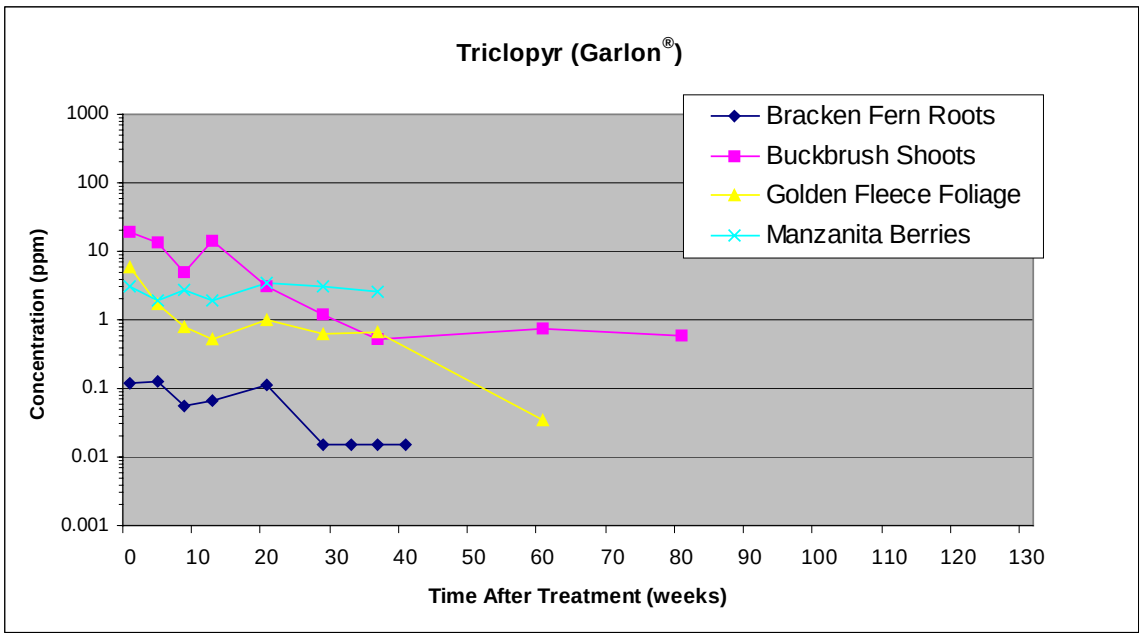
As to be expected, because of the differences in rate used, application methods employed (ground broadcast with granules versus direct liquid spray), plant parts sampled (aerial parts versus underground rhizomes) herbicides concentration in plants varied greatly.

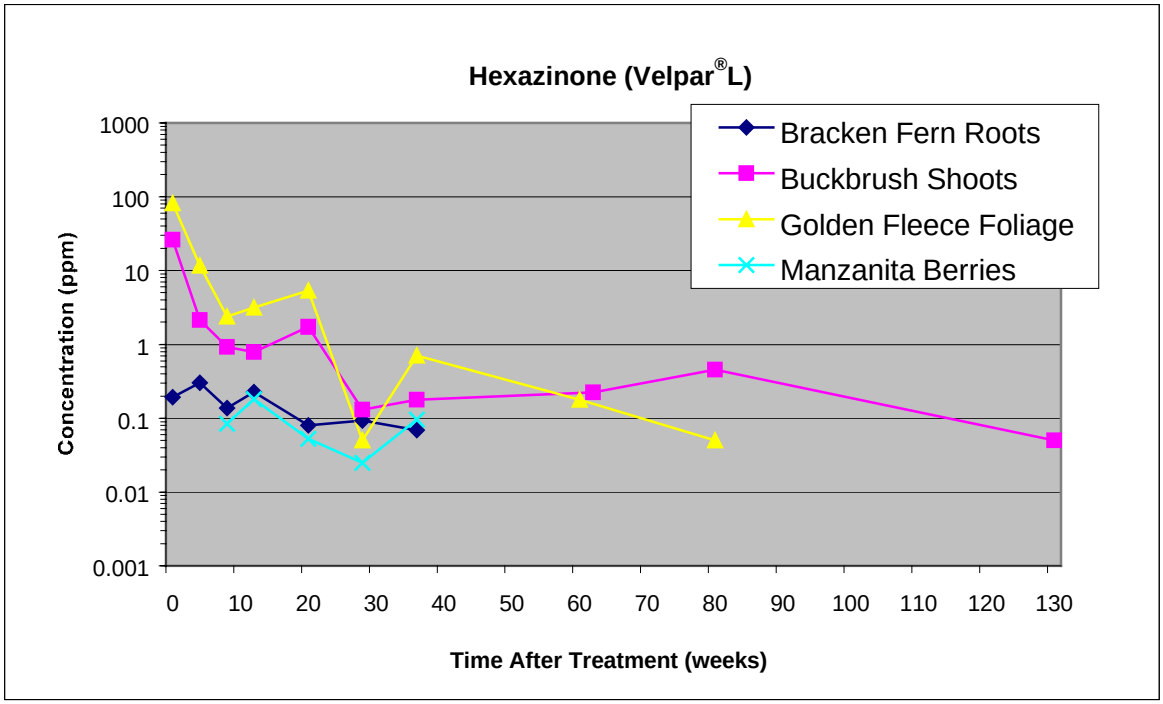
Glyphosate and triclopyr were detected up to 67 to 80 weeks after treatment, respectively. At this time, most of the plant materials were dead and decayed. Hexazinone residues were detected in buckbrush shoots up to 130 weeks after treatment. The available shoots throughout the sampling intervals were either in the final process of decaying or re-sprouting from plants that received lower dose of hexazinone from spraying variability. Sidhu and Feng (1993) showed similar trend in shrubs treated with hexazinone in a Canadian forest. The formulation has distinctive effect on the concentration of hexazinone found in plants. Foliar applied hexazinone (Velpar®) showed a declining trend from initial concentrations of 30 to 100 ppm (fresh weight) for shoots and foliage; while, the granular formulation (Pronone®) show a steady concentration of 1 ppm as the plant uptake the chemical from the soil (Fig 1). Although the plant materials in the treated area were dead, dying, chlorotic, brittle or deformed and hence are undesirable and very unlikely to be selected for basketweaving, medicine or food, we continued to monitor for herbicide residues until they were no longer detectable or no plants were available. However to be certain of avoiding plant materials with detectable herbicide residues, plants should not be gathered within 80 weeks of glyphosate and triclopyr applications. For hexazinone liquid or granular treated plants, they should not be gathered within 130 weeks of treatment.

Oak trees bearing acorns were only available in four sites treated with hexazinone and glyphosate. No herbicide residues were detected in any of the acorn samples. The analytical method reporting-limit for acorn was 0.1 ppm for both herbicides.

Figure 1. Field dissipation of herbicides on plants. Each sample represents the average concentration for a plant type collected from Stanislaus, Sierra and Eldorado National Forests, California 1997-2000






Hexazinone (Velpar®L)
Concentration (ppm)
1000
100
10
1
0.1
0.01
0.001
0
10
20
30
40
50
60
70
80
90
100
110
120
130
Time After Treatment (weeks)
Bracken Fern Roots
Buckbrush Shoots
Golden Fleece Foliage
Manzanita Berries

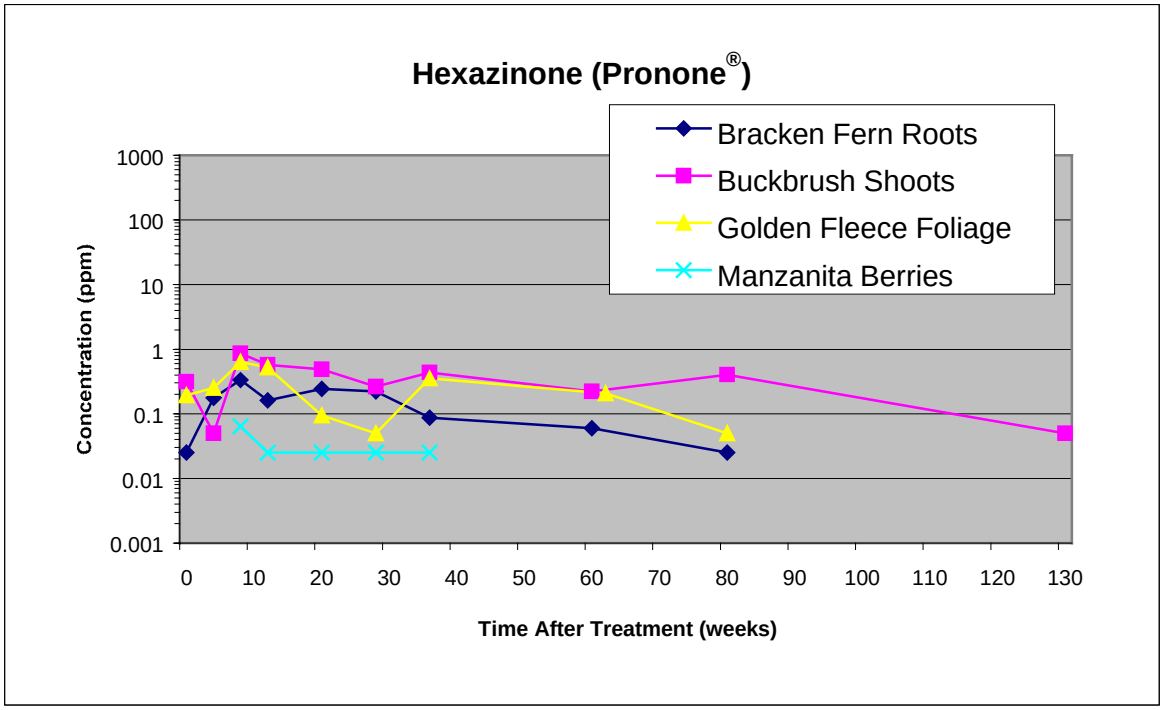

Hexazinone (Pronone®)
Concentration (ppm)
1000
100
10
1
0.1
0.01
0.001
0
10
20
30
40
50
60
70
80
90
100
110
120
130
Time After Treatment (weeks)
Bracken Fern Roots
Buckbrush Shoots
Golden Fleece Foliage
Manzanita Berries

Table 1. Offsite movement of herbicides at various times and distances from application at three national forests, 1997-2000.

Forest	District	Stand	Year Treated	Media	Chemical	Reporting Limit (PPM)	Post Application (weeks)	5-15 ft	20-40 ft	50-70 ft	80-100 ft
Eldorado	Pacific	501-120	1997	Deerbrush	Glyphosate	0.1	BK	NT	NT	NT	NT
Eldorado	Pacific	501-120	1997	Deerbrush	Glyphosate	0.1	0	ND	ND	ND	ND
Eldorado	Pacific	501-120	1997	Deerbrush	Glyphosate	0.1	4	ND	ND	ND	ND
Eldorado	Pacific	501-120	1997	Deerbrush	Glyphosate	0.1	12	ND	0.1-1	ND	ND
Eldorado	Pacific	501-120	1997	Deerbrush	Triclopyr	0.03	BK	NT	NT	NT	NT
Eldorado	Pacific	501-120	1997	Deerbrush	Triclopyr	0.03	0	ND	ND	ND	ND
Eldorado	Pacific	501-120	1997	Deerbrush	Triclopyr	0.03	4	ND	ND	ND	ND
Eldorado	Pacific	501-120	1997	Deerbrush	Triclopyr	0.03	12	ND	ND	ND	ND
Eldorado	Placerville	613-042	1998	Deerbrush	Glyphosate	0.1	BK	ND	ND	ND	ND
Eldorado	Placerville	613-042	1998	Deerbrush	Glyphosate	0.1	0	2.68	ND	ND	ND
Eldorado	Placerville	613-042	1998	Deerbrush	Glyphosate	0.1	4	0.121	ND	ND	ND
Eldorado	Placerville	613-042	1998	Deerbrush	Glyphosate	0.1	12	ND	ND	ND	ND
Eldorado	Placerville	613-042	1998	Deerbrush	Triclopyr	0.03	BK	ND	ND	ND	ND
Eldorado	Placerville	613-042	1998	Deerbrush	Triclopyr	0.03	0	1.56	0.07	0.06	0.03
Eldorado	Placerville	613-042	1998	Deerbrush	Triclopyr	0.03	4	ND	ND	ND	ND
Eldorado	Placerville	613-042	1998	Deerbrush	Triclopyr	0.03	12	ND	ND	ND	ND
Sierra	Kings River	S8	1999	Buckbrush	Glyphosate	0.1	BK	ND	ND	ND	ND
Sierra	Kings River	S8	1999	Buckbrush	Glyphosate	0.1	0	ND	ND	ND	ND
Sierra	Kings River	S8	1999	Buckbrush	Glyphosate	0.1	4	ND	ND	ND	ND
Sierra	Kings River	S8	1999	Buckbrush	Glyphosate	0.1	12	ND	ND	ND	ND
Sierra	Pineridge	336-149	1998	Buckbrush	Velpar	0.1	BK	ND	ND	ND	ND
Sierra	Pineridge	336-149	1998	Buckbrush	Velpar	0.1	0	ND	ND	ND	ND
Sierra	Pineridge	336-149	1998	Buckbrush	Velpar	0.1	4	ND	ND	ND	ND
Sierra	Pineridge	336-149	1998	Buckbrush	Velpar	0.1	12	ND	ND	0.673	ND
Sierra	Pineridge	Musick 071	1997	Buckbrush	Glyphosate	0.1	BK	ND	ND	ND	ND
Sierra	Pineridge	Musick 071	1997	Buckbrush	Glyphosate	0.1	0	0.1	ND	ND	ND
Sierra	Pineridge	Musick 071	1997	Buckbrush	Glyphosate	0.1	4	ND	ND	ND	ND
Sierra	Pineridge	Musick 071	1997	Buckbrush	Glyphosate	0.1	12	ND	0.11	ND	ND
Stanislaus	Groveland	025-055	1997	Bracken Fern	Pronone	0.05	BK	NT	NT	NT	NT
Stanislaus	Groveland	025-055	1997	Bracken Fern	Pronone	0.05	0	ND	ND	ND	ND
Stanislaus	Groveland	025-055	1997	Bracken Fern	Pronone	0.05	4	ND	ND	ND	Sample Lost
Stanislaus	Groveland	025-055	1997	Bracken Fern	Pronone	0.05	12	ND	ND	ND	ND
Stanislaus	Groveland	027-008	1997	Deerbrush	Velpar	0.1	BK	NT	NT	NT	NT
Stanislaus	Groveland	027-008	1997	Deerbrush	Velpar	0.1	0	ND	ND	ND	ND
Stanislaus	Groveland	027-008	1997	Deerbrush	Velpar	0.1	4	ND	ND	ND	ND
Stanislaus	Groveland	027-008	1997	Deerbrush	Velpar	0.1	12	ND	ND	ND	ND
Stanislaus	Groveland	027-013	1999	Buckbrush	Glyphosate	0.1	BK	ND	ND	ND	ND
Stanislaus	Groveland	027-013	1999	Buckbrush	Glyphosate	0.1	0	ND	ND	ND	ND
Stanislaus	Groveland	027-013	1999	Buckbrush	Glyphosate	0.1	4	ND	ND	ND	ND
Stanislaus	Groveland	027-013	1999	Buckbrush	Glyphosate	0.1	12	ND	ND	ND	ND

Forest	District	Stand	Sample Year	Media	Chemical	Reporting Limit (PPM)	Post Application (weeks)	5-15 ft	20-40 ft	50-70 ft	80-100 ft
Stanislaus	Groveland	027-054	1998	Deerbrush	Velpar	0.1	BK	ND	ND	ND	ND
Stanislaus	Groveland	027-054	1998	Deerbrush	Velpar	0.1	0	ND	ND	ND	ND
Stanislaus	Groveland	027-054	1998	Deerbrush	Velpar	0.1	4	ND	ND	ND	ND
Stanislaus	Groveland	027-054	1998	Deerbrush	Velpar	0.1	12	ND	ND	ND	ND
Stanislaus	Groveland	27-033	1998	Deerbrush	Velpar	0.1	BK	ND	ND	ND	ND
Stanislaus	Groveland	27-033	1998	Deerbrush	Velpar	0.1	0	ND	ND	ND	ND
Stanislaus	Groveland	27-033	1998	Deerbrush	Velpar	0.1	4	ND	ND	ND	ND
Stanislaus	Groveland	27-033	1998	Deerbrush	Velpar	0.1	12	ND	ND	ND	ND
Stanislaus	Mi-Wok	1171750	1998	Deerbrush	Glyphosate	0.1	BK	ND	ND	ND	ND
Stanislaus	Mi-Wok	1171750	1998	Deerbrush	Glyphosate	0.1	0	0.197	ND	ND	ND
Stanislaus	Mi-Wok	1171750	1998	Deerbrush	Glyphosate	0.1	4	0.101	ND	ND	ND
Stanislaus	Mi-Wok	1171750	1998	Deerbrush	Glyphosate	0.1	12	ND	ND	ND	ND
Stanislaus	Mi-Wok	1171750	1998	Deerbrush	Triclopyr	0.03	BK	ND	ND	ND	ND
Stanislaus	Mi-Wok	1171750	1998	Deerbrush	Triclopyr	0.03	0	0.03-0.3	0.03-0.3	0.03-0.3	ND
Stanislaus	Mi-Wok	1171750	1998	Deerbrush	Triclopyr	0.03	4	ND	ND	ND	ND
Stanislaus	Mi-Wok	1171750	1998	Deerbrush	Triclopyr	0.03	12	ND	ND	ND	ND
Stanislaus	Mi-Wok	11708407	1998	Deerbrush	Pronone	0.1	BK	ND	ND	ND	ND
Stanislaus	Mi-Wok	11708407	1998	Deerbrush	Pronone	0.1	0	ND	ND	ND	ND
Stanislaus	Mi-Wok	11708407	1998	Deerbrush	Pronone	0.1	4	ND	ND	ND	ND
Stanislaus	Mi-Wok	11708407	1998	Deerbrush	Pronone	0.1	12	ND	ND	ND	ND
Stanislaus	Mi-Wok	11720442	1998	Deerbrush	Pronone	0.1	BK	ND	ND	ND	ND
Stanislaus	Mi-Wok	11720442	1998	Deerbrush	Pronone	0.1	0	ND	ND	ND	ND
Stanislaus	Mi-Wok	11720442	1998	Deerbrush	Pronone	0.1	4	ND	ND	ND	ND
Stanislaus	Mi-Wok	11720442	1998	Deerbrush	Pronone	0.1	12	ND	ND	ND	ND
Stanislaus	Mi-Wok	033-138	1997	Bracken Fern	Pronone	0.05	BK	NT	NT	NT	NT
Stanislaus	Mi-Wok	033-138	1997	Bracken Fern	Pronone	0.05	0	ND	ND	ND	ND
Stanislaus	Mi-Wok	033-138	1997	Bracken Fern	Pronone	0.05	4	ND	ND	ND	ND
Stanislaus	Mi-Wok	033-138	1997	Bracken Fern	Pronone	0.05	12	ND	ND	ND	ND
Stanislaus	Mi-Wok	E061	1999	Buckbrush	Pronone	0.1	BK	ND	ND	ND	ND
Stanislaus	Mi-Wok	E061	1999	Buckbrush	Pronone	0.1	0	ND	ND	0.131	ND
Stanislaus	Mi-Wok	E061	1999	Buckbrush	Pronone	0.1	4	ND	ND	ND	ND
Stanislaus	Mi-Wok	E061	1999	Buckbrush	Pronone	0.1	12	ND	ND	ND	ND
Stanislaus	Mi-Wok	E121	1997	Buckbrush	Velpar	0.1	BK	NT	NT	NT	NT
Stanislaus	Mi-Wok	E121	1997	Buckbrush	Velpar	0.1	0	ND	ND	ND	0.124
Stanislaus	Mi-Wok	E121	1997	Buckbrush	Velpar	0.1	4	ND	ND	ND	ND
Stanislaus	Mi-Wok	E121	1997	Buckbrush	Velpar	0.1	12	ND	ND	ND	ND
Stanislaus	Mi-Wok	R041	1997	Deerbrush	Pronone	0.1	BK	NT	NT	NT	NT
Stanislaus	Mi-Wok	R041	1997	Deerbrush	Pronone	0.1	0	0.1-1	ND	0.1-1	ND
Stanislaus	Mi-Wok	R041	1997	Deerbrush	Pronone	0.1	4	ND	ND	ND	ND
Stanislaus	Mi-Wok	R041	1997	Deerbrush	Pronone	0.1	12	ND	ND	ND	ND

NT= sample not taken

ND= none detected

BK=pre-treatment background

Offsite Movement

Offsite movement of the four herbicide/formulations detected in the three national forests at various distances and in plant types is shown in Table 1. Nineteen out of the 253 samples taken from the 20 treated sites had detectable herbicide residues. As summarized in Table 2, this very low incidence (7.5%) of offsite movement occurred mostly within 70 feet from treated forest edge. This demonstrates that herbicides could be applied accurately to targeted area with hand held equipment such a backpack sprayer. Although granular hexazinone was applied by helicopter, there were only three detections from offsite samples. To be assured that there will be low probability of having residues in plant materials, gatherers should not collect within 100 feet from a treated area.

Table 2. Herbicides detected at various distances from the treated forest edge from Eldorado, Stanislaus, and Sierra National Forests, Calif. 1997-2000.

			No. of positive samples			
Herbicide	No. site	No. sample	5-15 ft	20-40 ft	50-70 ft	80-100 ft
Glyphosate	6	72	5	2	0	0
Triclopyr	3	36	2	2	2	1
Hexazinone (liquid)	5	60	0	0	1	1
Hexazinone (granules)	6	72	1	0	2	0

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Disclaimers

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