

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

Randy Segawa, Clarice Ando, Carissa Gana, and Kean S. Goh
Environmental Hazards Assessment Program
Department of Pesticide Regulation
830 K Street
Sacramento, CA 95814

Paul Lee, Duc Tran, Jane White, and Jean Hsu
Center for Analytical Chemistry
California Department of Food and Agriculture
3292 Meadowview Road, Sacramento, CA 95832

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 backpack sprayer or other ground equipment, or using helicopter to apply granular hexazinone where treatment areas are 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 report, we discuss the results of phase II study to date 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 US 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 chilled immediately and kept refrigerated until analysis.

In 1998, the following sites and application methods were monitored: Stanislaus National Forest sites were treated in March using all four herbicide/application methods; Sierra National Forest sites were treated in April using Velpar® L and Accord® by ground; and Eldorado National Forest sites were treated in June using Accord® and Garlon® by ground. The range 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, 209 samples were collected from 41 sites in the three National Forests representing the four plants and four treatment/application method combinations. For the off-site movement monitoring,

142 samples were collected from 13 sites at 5-15 ft, 20-40 ft, 50-70 ft and 80-100 ft from the edges of treated areas. Samples were collected immediately or within a day after treatment.

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 89 to 100%.

For hexazinone analysis, the plant homogenates were extracted with acetonitrile, cleaned up through solid phase extraction column, eluted with methanol/methylene chloride mixture. The extract was analyzed using an HPLC with ultraviolet detector. The reporting limit ranged from 0.05 to 0.2 ppm depending on plant type. Spiked sample recoveries ranged from 83 to 100%.

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 0.01 to 0.07 ppm, and spiked recoveries ranged from 79-100% depending on plant type.

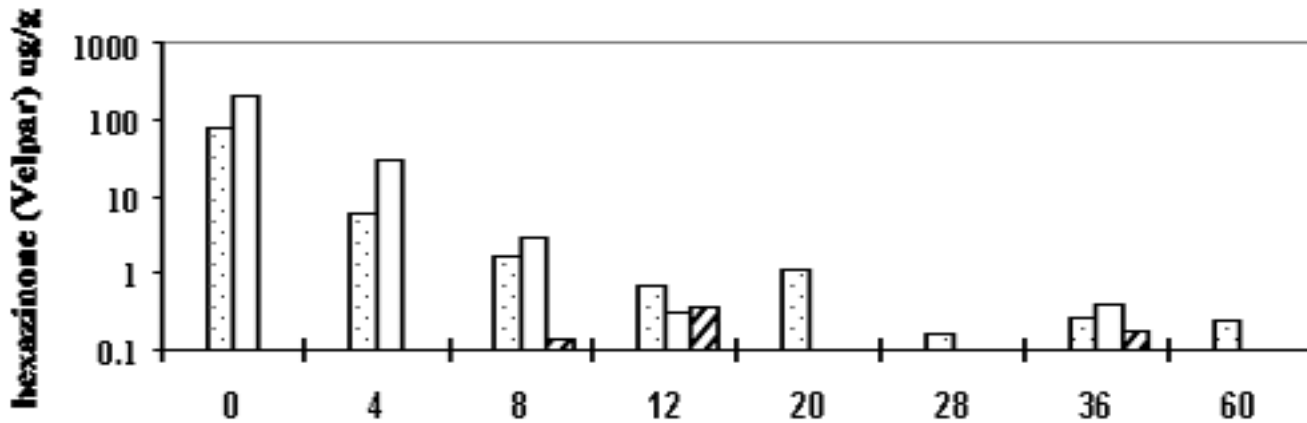
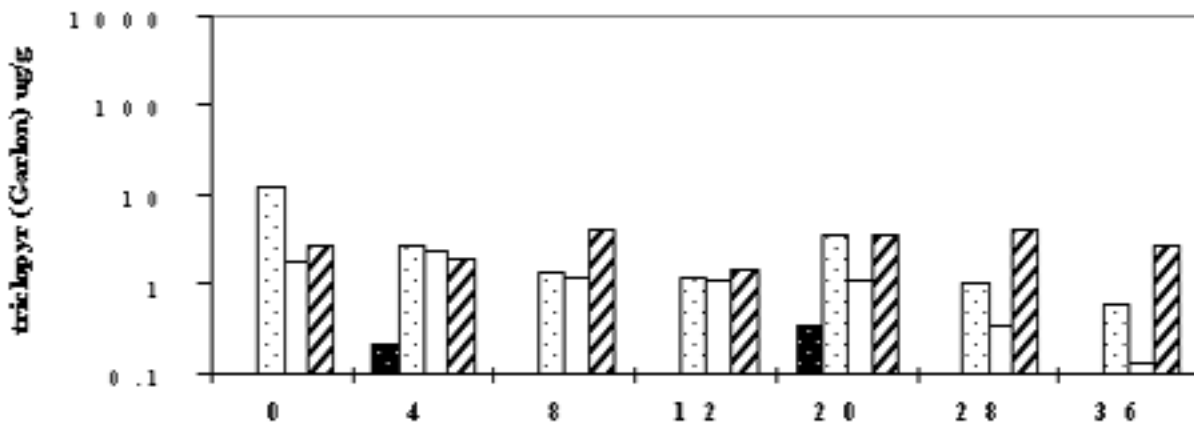
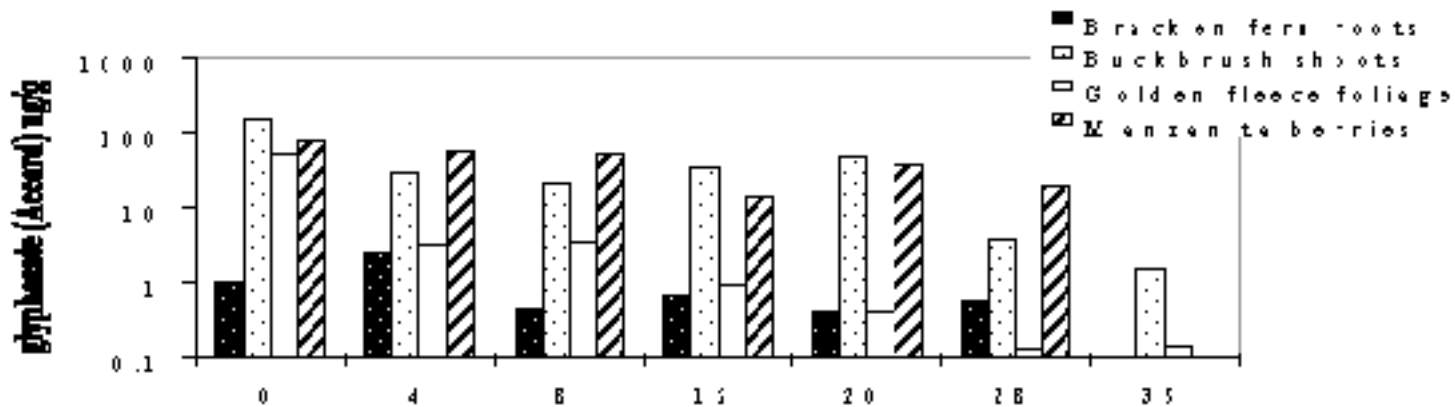
RESULTS AND DISCUSSION

Dissipation

For the dissipation study, a total of 209 plant samples from 41 treatment sites were collected among 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. For example, immediately after application concentrations varied from 122 ug/g in golden-fleece foliage for hexazinone liquid spray to non-detectable in bracken fern rhizomes in site treated with granular hexazinone. In Figure 1 the concentration detected for each plant and sampling date represents the highest detected concentration.

Glyphosate and triclopyr were detected at 36 weeks after treatment. At this time, most of the plant materials were dead and decayed. Hexazinone residues were detected in buckbrush shoots at 60 weeks after treatment (Fig. 1). The available shoots were either in the final process of decaying or re-sprouting from area that received lower dose of hexazinone. 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. Concentration of foliar applied hexazinone (Velpar®) showed a declining trend; while, the granular formulation (Pronone®) show a steady concentration of 1 ug/g 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 will continue to monitor for hexazinone residues in buckbrush until there are no longer detectable.



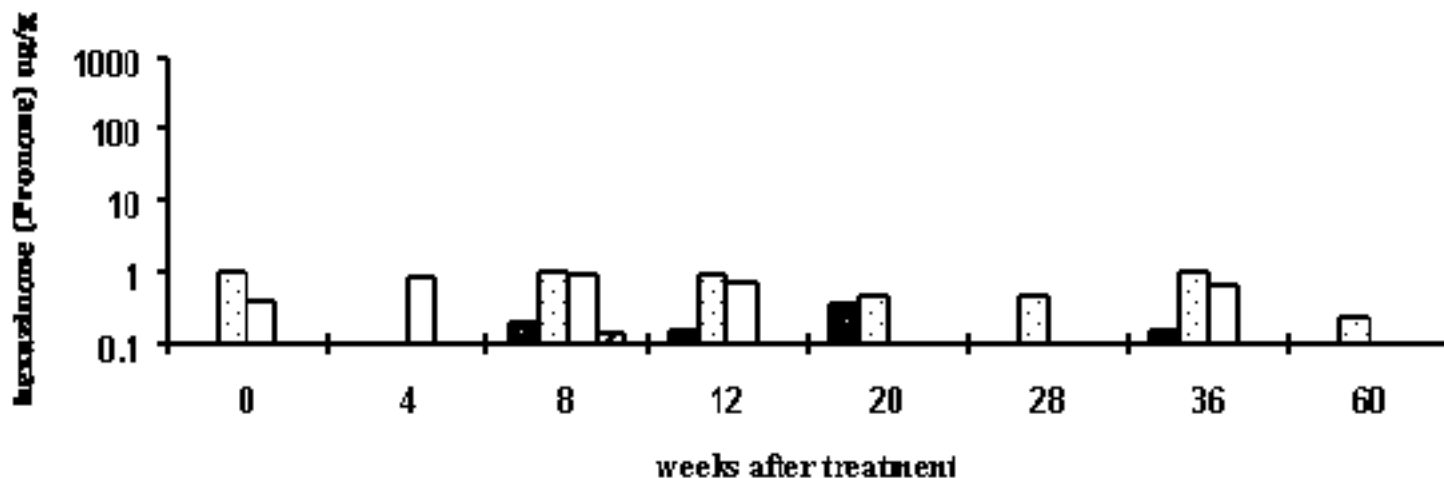


Figure 1. Dissipation of glyphosate, triclopyr, liquid hexazinone (Velpar), and granular hexazinone (Pronone) on four plants. Concentration at each sampling period represents the highest concentration detected in the plants.

Offsite Movement

Six out of the 142 samples taken from the 13 treated sites had detectable herbicide residues. As shown in Table 1, this very low incidence (4.2%) of offsite movement occurred mostly within 40 feet from treated forest edge. This demonstrate 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 no offsite movement detected. To be protective, gatherers should not collect plant materials within 100 feet from a treated area.

Table 1. Herbicides detected at various distances from the treated forest edge from Eldorado, Stanislaus, and Sierra National Forests, Calif. 1998.

Herbicide	no. sites sampled	no. of positive samples (no. of samples collected)			
		5-15 ft	20-40 ft	50-70 ft	80-100 ft
Glyphosate	2	1(6)	2(6)	0(6)	0(6)
Triclopyr	5	1(13)	0(13)	1(13)	0(12)
Hexazinone (liquid)	5	0(12)	0(12)	0(12)	1(12)
Hexazinone (granular)	1	0(3)	0(3)	0(3)	0(3)

REFERENCES

DiTomaso, J.M., D.B. Marcum, M.S. Rasmussen, E.A. Healy, G.B. Kyser. 1997. Post-fire herbicide sprays

enhance native plant diversity. Calif. Agric. 61:6-11.

Hutchens, A.R. 1991. Indian herbarology of North America. 382 pp. Shambhala Publication Inc. Boston, Mass. USA.

Segawa, R., A. Bradley, P. Lee, D. Tran, J. Hsu, J. White, and K.S. Goh. 1997. Residues of forestry herbicides in plants of importance to California Native Americans. Bull. Environ. Contam. Toxicol. 59:556-563.

Sidhu, S. S. and J. C. Feng. 1993. Hexazinone and its metabolites in boreal forest vegetation. Weed Sci. 41:281-287.

Strike, S.S. 1994. Ethnobotany of the California Indians. Vol. 2. Aboriginal uses of California's indigenous plants. Koeltz Scientific Books. USA.